Seogjoo J. Jang

Quantum Mechanics for Chemistry



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Seogjoo J. Jang
Chemistry and Biochemistry
Queens College, CUNY
Queens, NY, USA

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To my family

Preface

Modern chemistry was built on quantum mechanical foundations, but the amount of time allowed for chemistry students to learn both fundamental principles of quantum mechanics and details of its applications to molecular systems is very limited. Therefore, instruction of quantum mechanics in typical undergraduate and graduate chemistry curricula has been fairly limited in its depth. Rather, the focus of conventional physical chemistry or quantum chemistry education has been more on mastering facts and data resulting from applications of quantum mechanics that are essential for developing key chemical intuition and reasoning ability. However, in this age of unlimited accessibility to huge amount of data, the role of course instruction as a means to deliver comprehensive information can be relieved to a large extent. On the other hand, the need to lay a strong conceptual foundation remains irreplaceable and may have become even more important considering the demand for reasoning skills to assess information and data critically. This is the main motivation for writing this book.

As the title *Quantum Mechanics for Chemistry* suggests, this book intends to provide standard lessons on quantum mechanics as completely as possible, but also focuses on helping readers understand implications and applications of those lessons for molecular sciences. Thus, for example, standard lessons on quantum mechanical vibration, rotation, and hydrogen-like systems are combined with key principles and ideas of related spectroscopies in same chapters.

An important feature of this book is that the Dirac notation is introduced in a rather abstract manner and as completely as possible from the outset. This is because the Dirac notation serves as the most effective language to describe most quantum mechanical ideas and is the major notation being used for research level publications in physical chemistry and quantum chemistry.

Significant effort has also been made to provide clear quantum mechanical understanding of subtle and qualitative details of atomic and molecular properties, based on ideas and approximations that are as simple as possible. These lessons are then complemented by presentations of more advanced theories and computational methods in Appendices or later chapters of the book.

A unique feature of this book is that lessons that are not treated in most quantum chemistry textbooks such as general derivations of Fermi's golden rule, path integral approaches, and open system quantum dynamics theories are included while also providing reasonable description of electronic structure calculation theories. This is because new directions of research call for more balanced and comprehensive understanding of the structure, the energetics, and the dynamics of molecular systems altogether.

Intended readers of this book are upper level undergraduate chemistry students or beginning graduate students. Chapters 1–9 can be used as a text or reference for undergraduate level physical chemistry course. Chapters 1–11 can be used as a text for the first year graduate level quantum chemistry course. Chapter 12 is to provide preliminary lessons for those who plan to pursue theoretical and computational research in physical chemistry and chemical physics. This book can also be a useful reference for physics students and researchers who are interested in learning molecular quantum mechanics and quantum dynamics methods.

This book is an outcome of notes that I have developed for 17 years while teaching both undergraduate and graduate level quantum chemistry classes at Queens College and the Graduate Center of the City University of New York (CUNY), but major undertaking of writing this book started during the COVID-19 campus lockdown in 2020. Final completion of this book became possible through supports from the Korea Institute for Advanced Study (KIAS) for summer visit through its KIAS scholar program and from the Korea Advanced Institute of Science and Technology (KAIST), in particular the KAIX program, for my sabbatical stay in Fall 2022, during which I also taught a graduate level quantum chemistry course for students at KAIST.

Hardly anything presented in this book is original. Most standard contents were developed from textbooks and references that I used to learn and teach physical chemistry and quantum chemistry. Key references that I should mention here are Quantum Chemistry by McQuarrie [1], which was used for developing Chaps. 3–9; Quantum Chemistry by Levine [2], which served as an amazing reference for all the details of theories and methods that can be taught for quantum chemistry class; and Quantum Mechanics in Chemistry by Schatz and Ratner [3], which helped me learn broad subjects of quantum mechanics used in chemistry and also motivated the choice of the title of this book. In addition, many ideas for lessons originated from well-known books on quantum mechanics [4–8], group theory [9, 10], physical chemistry [11–13] quantum/computational chemistry [14, 15], and some books on advanced topics [16–18].

Completion of this book would not have been possible without assistances from Dr. Murali Devi who read manuscripts carefully and offered numerous valuable comments, Dr. Pablo Ramos who provided many key figures/illustrations and suggestions for improving Chap. 11, and Taner Ture who also provided many important figures and validated many equations. I also would like to thank all the students at Queens College and the Graduate Center of CUNY and at KAIST who took my classes and provided valuable feedbacks. In particular, YoungKyun

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Supports from the National Science Foundation, the Department of Energy, and the Camille Dreyfus foundation for my research and teaching all have made significant contributions to the development of this book. Encouragements and comments from my colleagues and intellectual mentors also have played important roles. In particular, I would like to thank Profs. George Schatz, Jeff Cina, Jae Woo Park, Weita Yang, and Greg Voth, and Dr. Qin Wu for their positive feedback and comments. Profs. Changbong Hyeon at KIAS and Young Min Rhee at KAIST are also appreciated for hosting my visits and valuable comments. I also would like to thank Sam Harrison of Springer Nature for generous consideration and encouragement of this book. Most of all, my family's support and love gave me lasting power to work on this book project.

Queens, NY, USA Seogjoo Julian Jang
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Physical Constants and Abbreviations

Table 1 contains important physical constants as follows.

Table 1 Physical constants in SI units from the NIST reference data

Constant	Symbol	SI units
Planck constant	h	$6.62607015 \times 10^{-34}$ J · s
Planck constant, reduced	$\hbar$	$1.054571817 \times 10^{-34}$ J · s
Speed of light	c	2.99792458×10^{8} m · s^{-1}
Boltzmann constant	k_B	1.380649×10^{-23} J · K^{-1}
Electron mass	m_e	$9.1093837015 \times 10^{-31}$ kg
Proton mass	m_p	$1.67262192369 \times 10^{-27}$ kg
Elementary charge	e	$1.602176634 \times 10^{-19}$ C
Rydberg constant	R_∞	$1.0973731568160 \times 10^{7}$ m^{-1}
Bohr radius	a_0	$5.29177210903 \times 10^{-11}$ m
Bohr magneton	β_B	$9.2740100783 \times 10^{-24}$ J · T^{-1}
Vacuum permittivity	ϵ_0	$8.8541878128 \times 10^{-12}$ C^{2}N^{-1}m^{-1}
Hartree	E_h	$4.3597447222071 \times 10^{-18}$ J

Unit Conventions

- **Atomic units (a.u.)** are in $\hbar$ (action), e (electric charge), a_0 (length), and m_e (mass). Thus, the unit energy in a.u. is $E_h = \hbar^2/(m_e a_0)$.
- **eV** is a unit of energy defined as electron charge e times volt (JC^{-1}). Thus, 1 eV $= 1.602176634 \times 10^{-19}$ J.
- **Wavenumber** (cm^{-1}) is energy divided by $hc = 1.98644586 \times 10^{-23}$ J·cm and is used as a unit of energy in spectroscopy. Thus, 1 eV $= 8.06554393 \times 10^{3}$ cm^{-1}.

Abbreviations

BO	Born-Oppenheimer
B.O.	Bond Order
CI	Configuration Interaction
DFT	Density Functional Theory
FGR	Fermi's Golden Rule
HF	Hartree-Fock
Irrep.	Irreducible Representation
LCAO-MO	Linear Combination of Atomic Orbitals as Molecular Orbital
MO	Molecular Orbital
POVM	Positive Operator Valued Measure
QME	Quantum Master Equation
SCF	Self-Consistent Field
TD-DFT	Time-Dependent Density Functional Theory

Chapter 1
Concepts and Assumptions of Quantum Mechanics



To exist is to be free from contradiction.

— Henri Poincare

Abstract This chapter introduces key concepts, major assumptions, and basic formulations of quantum mechanics. For contextual understanding, assumptions of classical mechanics are clarified first. Then, light quanta, material wave, and uncertainty principles are explained. The wavefunction and Schrödinger equation defined in a one dimensional space are introduced along with their major properties. The chapter concludes with a solution of a quantum particle in a one dimensional box in order to illustrate the major concepts and ideas of quantum mechanics.

1.1 Assumptions of Classical Mechanics

Before the development of quantum mechanics, classical mechanics was believed to explain the state and the dynamics of all physical objects. The assumption behind this belief was that it should be possible to represent any physical object as a collection of *classical point particles*, whereas fields such as electromagnetic waves act as agents for forces and are governed by laws that are also well understood.

1.1.1 Classical Point Particles

A point particle in classical mechanics is completely specified by its position and momentum that can be determined *simultaneously and precisely*. Then, such information can be used for solving the Newtonian equation of motion for the particle (or Hamilton's equations in more general terms), so as to *predict* or *retrodict* its position and momentum at another time. In other words, according to classical mechanics, the position and momentum of a point particle, once known completely at a given time, can be determined fully at any past or future time. The rest of issue

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in understanding the physical world then falls down to finding out the way a given object can be represented as a collection of point particles and determining all the forces (or potential energies) governing the dynamics of these particles.

For example, consider a point particle with mass m in one dimension. The position and momentum of this particle at a given time t are $x(t)$ and $p(t)$, respectively. Assuming that there are no other degrees of freedom interacting with this particle and that the force on this particle depends only on the value of position, they can be shown to satisfy the following coupled equations of motion:

$$\frac{dx(t)}{dt} = \frac{p(t)}{m}, \tag{1.1}$$

$$\frac{dp(t)}{dt} = F(x(t)) = -\left.\frac{dV(x)}{dx}\right|_{x=x(t)}, \tag{1.2}$$

where $V(x)$ is the potential energy of the particle at position x. Combination of the above two equations of motion results in the familiar Newtonian equation of motion involving the acceleration, $a(x(t)) = F(x(t))/m$.

Solving Eqs. (1.1) and (1.2) along with known values of position and momentum x_0 and p_0 at a certain time $t = t_0$, one can obtain the position and momentum at any other time, $x(t; x_0, p_0)$ and $p(t; x_0, p_0)$. This results in a completely deterministic trajectory of the particle in the abstract space of position and momentum, which is called *phase space*. Along the trajectory of the particle in phase space, the Newtonian equation of motion ensures that the following Hamiltonian of the particle remains a conserved quantity.[1]

$$H(x, p) = \frac{p^2}{2m} + V(x). \tag{1.3}$$

This can be proved directly using Eqs. (1.1) and (1.2) as follows:

$$\begin{aligned}\frac{d}{dt}H(x(t), p(t)) &= \left[\frac{dx(t)}{dt}\frac{\partial H(x,p)}{\partial x} + \frac{dp(t)}{dt}\frac{\partial H(x,p)}{\partial p}\right]_{x=x(t),p=p(t)} \\ &= \frac{p(t)}{m}\frac{dV(x(t))}{dx(t)} - \frac{dV(x(t))}{dx(t)}\frac{p(t)}{m} = 0. \end{aligned} \tag{1.4}$$

Thus, the trajectory determined by the Newtonian equation of motion is the one conserving the Hamiltonian, which in general can be considered as the energy of the particle expressed as a function of position and momentum.

At this point, it is important to note that the point particle, the limit of an object with negligible spatial extent, is a mathematical idealization in classical mechanics.

[1] For more general and complete account of classical mechanics, refer to advanced textbooks on classical mechanics, for example, by Goldstein [19].

However, for the description of realistic objects with significant spatial extent, it is possible to devise a limiting procedure that divides the body into as small volume elements as possible so that each of the volume element can be treated like a point particle. Thus, as long as any object can be represented by a collection of finite or infinite number of interacting point particles with precisely determinable positions and momenta, it should be possible to completely understand the state and dynamics of the object on the basis of classical mechanics.

The advance of chemistry and physics in late nineteenth century revealed that all materials consisted of interacting atoms and molecules that can serve as ultimate building blocks of point particles. Thus, the reality of the physical world as portrayed by classical mechanics appeared to be all but confirmed.[2] An important exception to such description was light, or more broadly, the electromagnetic field. For this, Maxwell has already compiled and refined four distinct equations, now known as Maxwell's equations, which provide a complete description of an electromagnetic field in space and time and the manner of its interaction with materials. However, the question of how electromagnetic waves interact with materials at the atomic and molecular level was never clearly understood. Furthermore, detailed properties of individual atoms and molecules and those of subatomic particles such as the electron and the proton had yet to be understood well.

1.1.2 Wave: Classical View

What is a wave? A wave is characterized by a periodic motion of amplitude, in general, both in time and space, which can be standing or traveling, regardless of whether we can see them directly or not. One of the simplest wave equation in one dimension is

$$\left(\frac{1}{v^2}\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2}\right)u(x,t) = 0, \tag{1.5}$$

which is a partial differential equation with $f(x \pm vt)$ as a general solution. A well-known class of functions that can represent these solutions are sine and cosine functions. For example, the following sine function can easily be shown to be the solution of the above equation:

$$u(x,t) = A\sin(k(x - vt)) = A\sin\left(2\pi(\frac{x}{\lambda} - \nu t)\right). \tag{1.6}$$

[2] Indeed, outcomes of many modern computational simulations have confirmed that much of material systems we know of can be accurately described in terms of classical mechanics for molecules represented as a set of interacting point particles as long as all forces are determined accurately.

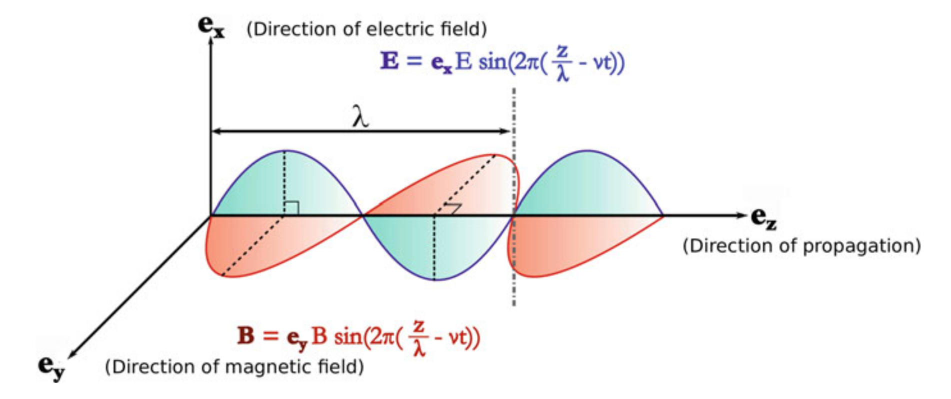


Fig. 1.1 Illustration of an electromagnetic field propagating along the z-direction with $\varphi = 0$

In the above expression, A is an amplitude, k is a wavevector, and v is the speed, or the magnitude of the phase velocity, of the wave, λ is wavelength, and ν is frequency. The above equation implies the following relationships between these quantities:

$$k = \frac{2\pi}{\lambda}, \tag{1.7}$$

$$\nu = \frac{kv}{2\pi}, \tag{1.8}$$

$$v = \lambda\nu. \tag{1.9}$$

The speed of the electromagnetic wave in vacuum, denoted as c, has the value of $2.99792458\cdots \times 10^{10}\mathrm{cm/s}$. If we define the direction of the propagation of the electromagnetic wave as the z-direction, the electric and magnetic field components of most commonly used forms[3] in vacuum are (see Fig. 1.1)

$$\mathbf{E} = \mathbf{e}_x E \sin\left(2\pi(\frac{z}{\lambda} - \nu t) + \varphi\right), \tag{1.10}$$

$$\mathbf{B} = \mathbf{e}_y B \sin\left(2\pi(\frac{z}{\lambda} - \nu t) + \varphi\right), \tag{1.11}$$

where $\mathbf{e}_x$ and $\mathbf{e}_y$ are directions along which the electric and magnetic field components oscillate, φ is an arbitrary phase factor, and the wavelength λ and frequency ν are related to the speed of light c through the following relationship:

$$c = \nu\lambda. \tag{1.12}$$

[3] These correspond to one particular polarization direction of traverse wave in Coulomb gauge.

For an electromagnetic wave, its mass and position cannot be defined like a classical point particle. However, a well-defined concept of the energy density for the wave, which is consistent with experimental results, exists. The energy of a wave is the energy associated with filling up the space with the wave. The exact expression for the energy density depends on the specific units of choice, but it can always be expressed as a linear combination of E^2 and B^2. Thus, the energy of the (classical) electromagnetic wave increases as the square of their amplitudes. For example, in Gaussian units, the energy density of an electromagnetic wave is

$$\mathcal{E} = \frac{1}{8\pi}\left(E^2 + B^2\right). \tag{1.13}$$

This expression implies that the energy of an electromagnetic wave depends on the square of its amplitude and can be made as small as possible. It turns out that abandoning this definition of energy density has become the starting point of quantum mechanics.

1.1.3 Particle Versus Wave

The dichotomy of the physical world into those of particles and waves, thus into full locality and non-locality, appeared to be intact until the late nineteenth century. However, with the progress of experimental capability, puzzling evidence that could not be explained in terms of known physical laws and concepts started to emerge. In retrospect, this is not surprising because the assumptions and concepts of classical mechanics and electromagnetism relied on observations of macroscopic phenomena, which then became idealized through mathematical abstraction. In fact, there was no guarantee that the physical behavior at atomic and molecular scale should obey the same law as those we observe with our senses directly.

Contrary to what was firmly believed, the key assumption of classical mechanics that (i) *both* position and momentum of any object can be determined *with arbitrary precision* had never been confirmed with sufficient accuracy for particles with very small mass. Another important assumption implicit in both classical mechanics and electromagnetism was that (ii) *the magnitude of the energy* of a particle or *the energy density* of an electromagnetic wave can be made *arbitrarily small in a continuous manner*, without restriction. Discoveries of subatomic particles such as the electron and the proton proved the existence of indivisible units in mass and charge, but it was still too difficult to test whether the two assumptions (i) and (ii) were valid for such particles in the early days of those discoveries. On the other hand, solid experimental findings for light and its interaction with electrons were recognized as not being consistent with classical theories, which made it necessary to examine the two assumptions (i) and (ii). It turned out that not only these assumptions but even the classical concept of particle versus wave needed to be altered in a fundamental manner, which then led to new concepts and ideas of quantum mechanics.

1.2 Concepts of Quantum Mechanics

1.2.1 Blackbody Radiation

What is light? How does light interact with matter? Pursuing answers for these questions has motivated the development of key concepts and principles of quantum mechanics. The beginning of this was Max Planck's success in explaining the energy distribution of light radiated from a blackbody.

A blackbody is a perfect absorber. The light that comes out of it is in full equilibrium with the body at a given temperature (see Fig. 1.2). The most puzzling experimental result concerning the blackbody radiation was that the measured *distribution of light energy intensity* in the high frequency region was drastically different from theoretical prediction based on Eq. (1.13). Experimentally, the light energy density reaches a maximum at certain frequency and decays to zero as the frequency increases. On the other hand, according to Eq. (1.13), such behavior is impossible to understand because the light wave should be packed more densely, namely with more modes of wave, as the frequency increases (wavelength decreases). This results in the energy density increasing as a quadratic function of its frequency, and thus leads to a hypothetical catastrophic behavior called ultraviolet divergence. On the other hand, the actual distribution of light energy coming from the blackbody has vanishing density as its frequency increases.

In an effort to solve the mystery of the blackbody radiation, Max Planck came up with an idea that *the energy of light emitted from a blackbody* is always quantized, which turned out to be one of the greatest discoveries in physics. He showed that the experimental data on blackbody radiation can be explained by a single assumption that the energy of light is an integer multiple of its frequency times a universal constant as follows:

$$E_{\text{light}} = nh\nu, \qquad n = 1, 2, \ldots, \tag{1.14}$$

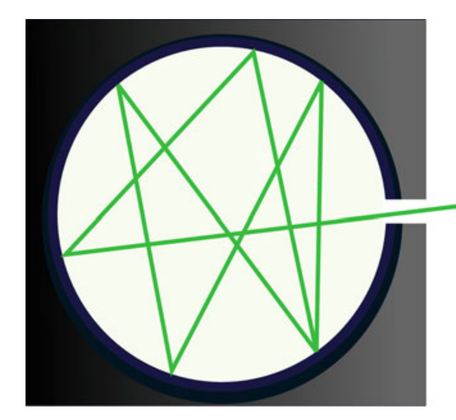


Fig. 1.2 Illustration of a blackbody. Light gets absorbed into the body and remitted numerous times before they make way out through the small hole

where $h = 6.626 \cdots \times 10^{-34}$ J · s and ν is the frequency of light. The fundamental constant h is now known as the Planck constant and can be considered as the unit of the action[4] of light.

Equation (1.14) represented a drastic departure from known concepts and principles that were believed to provide a complete description of light. It was firmly believe that the energy of light, as an electromagnetic wave fully describable by Maxwell's equations, can have arbitrary magnitude according to Eq. (1.13). However, this very assumption was simply an outcome of human perception of waves observable at macroscopic scale. In fact, the energy of light turned out to be a quantity that can be defined in a new way without affecting the validity of Maxwell's equations.

The acceptance of Eq. (1.14) even by Planck himself was a reluctant one. Initially, this was proposed as a remedy specific for fixing the "ultraviolet divergence" of the blackbody radiation. It was indeed possible to explain the blackbody radiation very accurately on the basis of Eq. (1.14), after accounting for some effects of statistical and geometric factors. As yet, Planck himself at the time of this discovery was not sure whether Eq. (1.14) was due to the specific nature of interaction between heated oscillators within the blackbody and the light trapped inside or whether it indeed represents an intrinsic property of light.

1.2.2 Photoelectric Effect and Photon

The simplest interpretation of Eq. (1.14) is that light is a collection of independent particles, each with energy $h\nu$. Albert Einstein used this concept of "packets of light" energy, which were named as photons later, and successfully explained a photoelectric effect that was difficult to understand with classical theories.

When light hits a metal surface, some electrons can be ejected from the surface. If one assumes that such phenomenon occurs as a result of the activation of electrons in metal surface by the driving of classical electromagnetic field, the ejection of the electron should depended entirely on the intensity of light. However, the experimental observation was that only the number of ejected electrons depended on the intensity of light. Careful analyses of experimental results established that (1) *whether electrons are ejected or not* and (2) the *magnitude of the kinetic energy of the ejected electron* depended only on the *frequency* of light, not the intensity of light. These can be summarized by the following relationship:

[4] Action is a rather abstract physical quantity originally introduced in a reformulation of Newtonian Mechanics and is defined as the product of momentum and position or that of energy and time. In other words, it is a cumulation of the energy of a certain physical "action" over certain duration of time.

$$h\nu = \frac{1}{2}m_e v^2 + \Phi, \tag{1.15}$$

where ν is the frequency of the incident light, m_e is the mass of electron, v is the speed of ejected electron, and Φ is the work function of the metal.

Both the blackbody radiation and the photoelectric effect can be explained in the simplest possible manner by assuming that light indeed consists of independent photons, each with energy $h\nu$. Then, what is the implication of this interpretation with regard to all other existing experimental evidences supporting the wave-nature of light? Since the two views of light as wave and particle are based on well-established experimental evidences, one compromising solution is that light can be viewed as either particle or wave depending on experimental condition and measurement type. But is this logically possible? It turns out that the answer for this can be yes as long as each photon retains the full characteristics of wave.

Once the notion of photon as a light particle is accepted,[5] the natural question that arises is what is its physical properties. First, the energy of a single photon is simply given by

$$\mathcal{E}_{ph} = h\nu. \tag{1.16}$$

Since light has zero rest mass and travels with a constant speed c in vacuum, the same property should be shared by each photon. According to the theory of relativity, the momentum of light with energy E is given by E/c. Therefore, it is easy to find that the momentum of a photon is given by

$$p_{ph} = h\frac{\nu}{c} = \frac{h}{\lambda}, \tag{1.17}$$

where λ is the wavelength of the photon. Thus, there is an inverse relationship between the momentum and the wavelength of a photon.

1.2.3 de Broglie's Postulate of Material Wave

Considering that light can be viewed as either wave or particle depending on the physical situation, it is natural to ask whether the same is true for objects that have been established as particles. If that is the case, what would be the characteristics of such a wave? Equation (1.17) shows that there is clear relationship between momentum and wavelength for the case of a photon. Can this relationship also

[5] However, the meaning of photon and the necessity to define it had been debated even after full development of quantum theory because most interaction with light could be explained in terms of assumption of classical wave before the advance of laser and modern quantum optics experiments [20].

be used for any particle? Indeed, de Broglie suggested that it can be used for any material, and supposed the existence of material wave with the following wavelength:

$$\lambda_{dB} = \frac{h}{p}, \tag{1.18}$$

where p is the magnitude of the momentum of the particle.

de Broglie's suggestion of Eq. (1.18) was extraordinary in the sense that it was made without any experimental backing at all. Soon it became a reality through confirmation by the Davisson-Germer's experiment [21], according to which a beam of electrons passing through a nickel foil showed diffraction pattern corresponding to a wave with the de Broglie wavelength of an electron. Even with such confirmation, the full physical meaning of de Broglie's material wave remained unclear, except that it linked particle with some kind of wave properties. Genuine understanding of this required development of a comprehensive theory.

As will be detailed later in this book, de Broglie's material wave also serves as a good justification for Bohr's quantization rule for explaining energy levels of an electron in a hydrogen atom. It can also serve as an essential component for proving and demonstrating Heisenberg's uncertainty principle. Most importantly, it can be viewed as the precursor of Schrödinger's theory of wave mechanics, now known as quantum mechanics.

1.2.4 Heisenberg's Uncertainty Principle

Upon further reflection on the nature of physical observables from a deeper philosophical viewpoint, namely, from the view that any given physical observable has its true meaning only to the extent of "definite experiment" by which it can be determined, Heisenberg reached a conclusion that there has to be an intrinsic limit in the accuracy of the position and the momentum that can be determined simultaneously. His initial estimate was that the lower limit for the simultaneous indeterminacy or uncertainty is $\Delta x \Delta p \sim h$, where Δx and Δp are uncertainties of the values of the position and momentum. This relationship is also consistent with de Broglie's theory given that $\Delta x \sim \lambda_{dB}$ and $\Delta p \sim p$.

Heisenberg recognized that the uncertainty is a fundamental limit that cannot be overcome by any improvement of experimental precision. He viewed this as the only way for *the principle of causality*, a fundamental cornerstone in any scientific reasoning, not to be violated while accepting wave-like nature of particle. Heisenberg also came up with a similar relationship between the energy and time, namely, that the minimum of the product of uncertainties of the energy and time is about $\Delta E \Delta t \sim h$. However, the physical origin and interpretation of this is different from that between position and momentum. Following a suggestion by Niels Bohr,

who strongly believed this as reflecting the dual nature of particle-like and wave-like properties that quantum objects have, Heisenberg termed these relationships as the uncertainty principle.

An exact statement of the uncertainty principle, which was clarified later through a well-defined mathematical analysis, corresponds to the following inequality:

$$\Delta x \Delta p \geq \frac{\hbar}{2}, \tag{1.19}$$

where $\hbar = h/(2\pi) = 1.0551 \cdots \times 10^{-34} Js$. In the above expression, Δx and Δp are defined as standard deviations from average values of position and momentum being measured at the same time. In fact, this relationship is not confined to only between position and momentum. Similar relationships can be found for any pair of observables that cannot be determined simultaneously.

1.2.5 Wave-Particle Duality

Niels Bohr's contribution to quantum mechanics goes far beyond the model of a hydrogen atom.[6] He laid out a fundamental conceptual basis for quantum mechanics along with Max Born by developing a key concept of the *duality of particle and wave nature*. He viewed that the concepts of particle and wave, taken separately, are not sufficient for describing physical phenomena in the quantum limit, but that they rather have to be combined together for a full description because they in fact play *complementary* roles.

The concept of *wave-particle duality* is easy to misunderstand or misinterpret. Even what Bohr meant by this remains not fully understood because he never agreed with others' interpretation of his view on this concept [22]. It is however easy to say what it is not. The concept of duality certainly does not imply that a small object such as electron suddenly becomes particle or wave depending on physical situation and the type of measurement. This would break the *principle of causality*, which ensures that *there is objective reality that proceeds by a well-defined cause and effect relationship*, a principle that serves as one of the two most important cornerstones of physics along with that of energy conservation.

In order for the concept of wave-particle duality to be consistent with the principle of causality, both properties of particle and wave should remain as intrinsic possibilities that can show up when an appropriate projection (measurement) is made while being governed by an objective causal relationship. It is important to recognize that the concepts of particle and wave are born out of human perception of the physical world, and are not guaranteed to be the best means to describe

[6] We will go through more details of this when we study hydrogen-like systems.

the quantum phenomena. Understanding what the duality really means remains an important philosophical question that goes beyond the scope of this book.

At the minimum, the duality means that we should abandon the simple concept of particle and wave that can be visualized easily as in classical theories. Rather, it is much more convenient to assume that there is a certain quantum state with unknown characteristics to be specified, which appear to have particle-like properties or wave-like properties depending on the types of physical measurement being made. Heisenberg assumed that such a quantum state can be represented by a complex valued vector in an abstract space. On the other hand, Schrödinger introduced a wavefunction, which turned out to embody the dual nature of particle and wave in the most precise way. This will be described in more detail in the following section.

1.3 Schrödinger Equation (in One Dimension) and Probability Amplitude

Shortly after Heisenberg developed the theory of quantum mechanics in terms of matrix equations, Schrödinger completed an alternative mathematical theory by introducing the concept of wavefunction, which represents a general quantum mechanical state, and identifying a powerful partial differential equation that allows its full specification.

1.3.1 Wavefunction and Time Dependent Schrödinger Equation

Given a wavefunction $\psi(x, t)$, a complex valued function of position and time, representing a quantum mechanical state of an object or system, the time dependent Schrödinger equation that determines its time evolution in one dimension is given by

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) + V(x)\psi(x,t), \tag{1.20}$$

where m is the mass of the object that the wavefunction represents and $V(x)$ is the potential energy it is subject to. This potential energy is assumed to be time independent in the above expression but can be extended to time dependent cases.

The peculiar nature of $\psi(x, t)$ is that it is in general a complex valued function. An example is $e^{ikx-i\omega t} = \cos(kx - \omega t) + i\sin(kx - \omega t)$. The physical meaning of the wavefunction has been under intense debate during the formative period of quantum mechanics. The standard interpretation that is now well-established is that $\psi(x, t)$ gives the probability to find a quantum mechanical particle as prescribed below.

Implication and Properties of Wavefunction

For a system represented by a wavefunction with its value $\psi(x, t)$ at x and at time t, the probability to find the system is as follows:

$|\psi(x, t)|^2 dx$: Probability to find the system between x and $x + dx$ at time t

It is important to note that the above interpretation is consistent with the concept of the wave-particle duality and the principle of causality. The former is ensured by the probabilistic nature of the wavefunction and the latter is guaranteed by the fact that the time dependent Schrödinger equation governs its time evolution deterministically.

There are two important properties a wavefunction should satisfy.

- A wavefunction for a bounded system is normalized[7] as

$$\int_R |\psi(x, t)|^2 dx = 1, \tag{1.21}$$

  where R is the region where the wavefunction is defined. The normalization condition exists because the total probability has to be equal to one.
- A wavefunction should be continuous in space. This is because the probability density has to be defined uniquely at any point in space. It is important to note that the wavefunction becomes zero in the region where the potential becomes infinite.

[7]Bounded system means that the potential energy renders the particle to be localized at a region of finite volume. For unbounded systems, a different convention for normalization is used.

1.3.2 *Measurement as Mathematical Operation on Wavefunction*

An important assumption in Schrödinger's formulation is that measuring a physical property of a quantum mechanical state can be represented by a "mathematical" operation on the wavefunction. For example, the operation corresponding to a position measurement is represented by the following simple multiplication:

$$\hat{x}\psi(x, t) = x\psi(x, t). \tag{1.22}$$

In the same way, measuring any function of position $A(x)$ simply amounts to multiplication with this function. In other words, the operation of $\hat{A}(\hat{x})$ is defined as

$$\hat{A}(\hat{x})\psi(x,t) = A(x)\psi(x,t). \tag{1.23}$$

Note that $x\psi(x,t)$ and $A(x)\psi(x,t)$ are not constant multiples of $\psi(x,t)$ in general. Thus, measurement of this position dependent physical observable changes the quantum state in general. The exception for this is when the wavefunction is fully localized at one specific point, for which a special definition of function is needed as will become clear later in this chapter.

On the other hand, the measurement of momentum turns out to be a differentiation given by

$$\hat{p}\psi(x,t) = \frac{\hbar}{i}\frac{\partial}{\partial x}\psi(x,t). \tag{1.24}$$

For the case where $\psi(x,t) \sim e^{ikx-i\omega t}$, which represents a complex valued wave with definite wavelength $\lambda = 2\pi/k$, the above definition results in the following value for the momentum:

$$p = \hbar k = \frac{h}{2\pi}\frac{2\pi}{\lambda} = \frac{h}{\lambda}. \tag{1.25}$$

Thus, Eq. (1.24) is consistent with de Broglie's postulate of a material wave.

Classically, the kinetic energy is given by $p^2/(2m)$. This definition can be used to define quantum mechanical kinetic energy operator as

$$\hat{K} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \tag{1.26}$$

The combination of Eq. (1.23), with $V(x)$ for $A(x)$, and Eq. (1.26) leads to a compact expression for the time dependent Schrödinger equation (1.20) as summarized below.

Time-Dependent Schrödinger Equation and Hamiltonian

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = \hat{H}\psi(x,t), \tag{1.27}$$

where $\hat{H}$ is the Hamiltonian operator defined as

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x). \tag{1.28}$$

(continued)

The implication of this is that the Hamiltonian operator generates the time evolution of the wavefunction. Thus, information on the Hamiltonian and the wavefunction at a given time $t = t_0$ allows determination of the quantum state at any time.

1.3.3 Stationary States and Time Independent Schrödinger Equation

Let us define a stationary quantum mechanical state $\psi_s(x,t)$ as the one satisfying the following relationship:

$$i\hbar\frac{\partial}{\partial t}\psi_s(x,t) = E\psi_s(x,t). \tag{1.29}$$

Let us also assume that the dependences of the wavefunction on position and time can be decoupled from each other as follows: $\psi_s(x,t) = \psi(x)f(t)$. Inserting this relation into the above equation, we obtain

$$i\hbar\frac{df(t)}{dt}\psi(x) = Ef(t)\psi(x). \tag{1.30}$$

For nonzero $\psi(x)$, the above relation implies that

$$\frac{df(t)}{dt} = -\frac{iE}{\hbar}f(t), \tag{1.31}$$

the solution of which is $f(t) = f(0)e^{-iEt/\hbar}$. Let us now assume that the time independent part of the wavefunction is equal to the full time dependent wave function at $t = 0$. That is, $\psi(x) = \psi_s(x,0)$. Then, $f(0) = 1$ and

$$f(t) = e^{-iEt/\hbar}. \tag{1.32}$$

Inserting $\psi_s(x,t) = f(t)\psi(x)$, with the above expression for $f(t)$, into Eq. (1.29), we obtain

$$\hat{H}\psi(x) = E\psi(x). \tag{1.33}$$

Thus, for a special kind of wavefunction $\psi(x)$ that satisfies the above equation, the corresponding time dependent wavefunction that satisfies Schrödinger's time dependent equation, Eq. (1.27), is obtained by simply multiplying it with $e^{-iEt/\hbar}$.

Time Independent Schrödinger Equation and Eigenvalue of Hamiltonian

Equation (1.33) is known as time independent Schrödinger equation and can be used for complete specification of all the stationary states and corresponding energies for a given Hamiltonian. Not all wavefunctions and energy E satisfy this equation. In fact, this is an eigenvalue problem, for which both E and $\psi(x)$ should be determined. Let us denote the wavefunction satisfying Eq. (1.33) for a specific value of E as $\psi_E(x)$. Namely,

$$\hat{H}\psi_E(x) = E\psi_E(x). \tag{1.34}$$

Mathematically, $\psi_E(x)$ is called an eigenfunction of the Hamiltonian operator with eigenvalue E. Physically, what this means is that, if the energy is measured for a system represented by $\psi_E(x)$, the state is not disturbed and the result of the energy measurement is the value of E. For a given Hamiltonian, there is a well-defined set of finite or infinite eigenfunctions and eigenvalues, the determination of which amounts to fully solving the time independent Schrödinger equation.

1.3.4 Eigenfunction and Eigenvalue

Eigenfunction and eigenvalue are general mathematical terms that are not necessarily limited to quantum mechanics. For any mathematical operator $\hat{O}$ satisfying the following condition:

$$\hat{O}\psi_\lambda(x) = \lambda\psi_\lambda(x), \tag{1.35}$$

one can call $\psi_\lambda(x)$ as an eigenfunction of $\hat{O}$ with eigenvalue λ. Solving this eigenvalue problem is often the major step for finding a general solution involving the operator $\hat{O}$.

Even within quantum mechanics, eigenfunction and eigenvalue are not limited to the Hamiltonian operator but can also be defined for other physical observables. For example, consider $\phi_k(x) = e^{ikx}$, where k is a real number. Then,

$$\hat{p}\phi_k(x) = \frac{\hbar}{i}\frac{\partial}{\partial x}e^{ikx} = \hbar k e^{ikx} = \hbar k \phi_k(x). \tag{1.36}$$

The above relation shows that $\phi_k(x)$ is an eigenfunction of the momentum operator with eigenvalue $\hbar k$. In other words, $\phi_k(x)$ represents a quantum mechanical state with a definite momentum $\hbar k$.

For a quantum particle moving freely in space without any potential energy, the Hamiltonian operator is

$$\hat{H}_{fp} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}. \tag{1.37}$$

Then,

$$\hat{H}_{fp}\phi_k(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}e^{ikx} = \frac{\hbar^2 k^2}{2m}e^{ikx}. \tag{1.38}$$

This shows that $\phi_k(x)$ is also an eigenfunction of $\hat{H}_{fp}$ with eigenvalue $\hbar^2 k^2/(2m)$.

On the other hand, if there is nonzero potential $V(x)$, $\phi_k(x)$ no longer becomes the eigenfunction of the Hamiltonian as shown below.

$$\hat{H}\phi_k(x) = \left(\frac{\hbar^2 k^2}{2m} + V(x)\right)\phi_k(x) \neq \lambda\phi_k(x), \text{ for any } \lambda \tag{1.39}$$

As the above equation indicates, $\phi_k(x)$ is not an eigenfunction of $\hat{H}$ for nonzero potential because $V(x)\phi_k(x)$ cannot be a constant multiple of $\phi_k(x)$.

1.3.5 Linear and Hermitian Operator

For any physically measurable quantity, there should be a well-defined operator for which eigenvalues and eigenfunctions can be identified. However, it is important to note that not all kinds of mathematical operators can be used to represent a physical observable.

First, it is assumed that *any operator corresponding to physical observable is linear*. The definition of a linear operator is as follows.

Definition of Linear Operator

An operator acting on a set of complex functions, $\mathcal{F}$, is called linear, if for any functions $f_1(x)$ and $f_2(x)$ belonging to $\mathcal{F}$ and complex coefficients c_1 and c_2, the following identity always holds:

$$\hat{O}(c_1 f_1(x) + c_2 f_2(x)) = c_1\hat{O}f_1(x) + c_2\hat{O}f_2(x). \tag{1.40}$$

The above definition implicitly assumes that any linear combination (with complex coefficients) of functions belonging to $\mathcal{F}$ still remains in $\mathcal{F}$. It is easy to show that the position, momentum, and Hamiltonian operators are all linear operators.

Second, the eigenvalues of operators corresponding to physical observables have to be *real-valued* because no physical measurement can produce complex numbers. A class of operators called Hermitian operators guarantee this property. Therefore, *all operators corresponding to physical observables are assumed to be Hermitian*. The definition of a Hermitian operator is as follow.

Definition of Hermitian Operator

An operator $\hat{A}$ that acts on a complex valued function of one dimensional variable x is called Hermitian if it satisfies the following identity for any complex valued functions $\phi(x)$ and $\psi(x)$:

$$\int_R dx\ \phi^*(x)\hat{A}\psi(x) = \left(\int_R dx\ \psi^*(x)\hat{A}\phi(x)\right)^*, \tag{1.41}$$

where R represents the domain of x where the functions are defined (including its boundary condition) and $(\cdots)^*$ denote complex conjugate. It is assumed that the operator $\hat{A}$ acts on the function on its righthand side.[8] The above definition can be extended to functions of multi-variables by simply extending the integration to corresponding multi-dimensional integration.

[8]More generally, it is possible to define an operator acting on the function on the lefthand side, for which the definition of a Hermitian operator remains the same.

It is easy to show that the position operator and any function of position operator are Hermitian. The proof that momentum operator is a Hermitian operator can also be proved employing integration by parts given that the boundary terms do not contribute. The fact that the eigenvalue of a Hermitian operator is a real number can be shown easily as follows.

Theorem 1.1 *If $\phi_\lambda(x)$ is an eigenfunction of a Hermitian operator $\hat{A}$, its eigenvalue λ is always a real number.*

Proof By employing $\psi(x) = \phi(x) = \phi_\lambda(x)$ on the lefthand side of Eq. (1.41) and using the fact that $\hat{A}\phi_\lambda(x) = \lambda\phi_\lambda(x)$, we obtain

$$\int_R dx\ \phi_\lambda^*(x)\hat{A}\phi_\lambda(x) = \lambda\int_R dx\ \phi_\lambda^*(x)\phi_\lambda(x) = \lambda\int_R dx\ |\phi_\lambda(x)|^2 \tag{1.42}$$

On the other hand, using the same definitions and identity on the righthand side of Eq. (1.41), we also obtain

$$\left(\int_R dx\ \phi_\lambda^*(x)\hat{A}\phi_\lambda(x)\right)^* = \left(\lambda\int_R dx\ \phi_\lambda^*(x)\phi_\lambda(x)\right)^* = \lambda^*\int_R dx\ |\phi_\lambda(x)|^2, \tag{1.43}$$

where the fact that $\int_R dx\, \phi_\lambda^*(x)\phi_\lambda(x)$ is a real number has been used. Since the fact that $\hat{A}$ is Hermitian implies that Eqs. (1.42) and (1.43) are the same and because $\int_R dx\, \phi_\lambda^*(x)\phi_\lambda(x)$ is nonzero, we find that $\lambda = \lambda^*$. Thus, λ is a real number. □

1.3.6 Results of Measurement and Expectation Value

When a quantum system is in an eigenstate of a physical observable $\hat{A}$, the result of the measurement is always the corresponding eigenvalue. What if the state is not any of the eigenstates? Then, the result of the measurement is not certain. However, even in this case, *a possible value of individual measurement result is always one of the known eigenvalues* of $\hat{A}$.

To be more specific, let us assume that the state of the system at a certain time is $\psi(x)$ and the eigenstates of $\hat{A}$ are $\phi_j(x)$'s with eigenvalues A_j's, where j is an index labeling the eigenstates. Then, the statement given above can be represented by the following probability for the result of the measurement made for the state $\psi(x)$ to be the eigenvalue A_j:

$$p_j(\psi) = \left| \int_R dx\, \phi_j^*(x)\psi(x) \right|^2. \tag{1.44}$$

In case $\psi(x)$ is $\phi_j(x)$, this probability is equal to one because $\phi_j(x)$ is normalized. Thus, the measurement result is always A_j. In case $\psi(x)$ is $\phi_k(x)$ for different $A_k \neq A_j$, it is logically clear that this probability should be zero. This is possible only if

$$\int_R dx\, \phi_j^*(x)\phi_k(x) = 0, \text{ for } A_j \neq A_k. \tag{1.45}$$

This can be proved using the fact that $\hat{A}$ is Hermitian as follows.

Theorem 1.2 *Two eigenfunctions of a Hermitian operator with different eigenvalues are always orthogonal to each other.*

Proof Equation (1.41) for the case of $\phi_j(x)$ and $\phi_k(x)$ becomes

$$\int_R dx\, \phi_j^*(x)\hat{A}\phi_k(x) = \left(\int_R dx\, \phi_k^*(x)\hat{A}\phi_j(x) \right)^*. \tag{1.46}$$

Since $\hat{A}\phi_k(x) = A_k\phi_k(x)$ and $\hat{A}\phi_j(x) = A_j\phi_j(x)$, the above relation implies that

$$A_k \int_R dx\, \phi_j^*(x)\phi_k(x) = \left(A_j \int_R dx\, \phi_k^*(x)\phi_j(x) \right)^*. \tag{1.47}$$

Since A_j is a real number and $(\phi_k^*(x)\phi_j(x))^* = \phi_k(x)\phi_j^*(x)$, the above identity implies that

$$(A_k - A_j)\int_R dx\ \phi_j^*(x)\phi_k(x) = 0. \tag{1.48}$$

Since $A_k - A_j \neq 0$, the above identity is equivalent to Eq. (1.45). □

Let us consider more general case where the wavefunction is given by a linear combination of different $\phi_k(x)$'s for which all the eigenvalues A_k's are different as follows:

$$\psi(x) = \sum_k C_k\phi_k(x), \tag{1.49}$$

where C_k's are complex coefficients that can be arbitrary except for the constraint that $\sum_k |C_k|^2 = 1$. The reason for this constraint will soon become clear. Employing Eq. (1.44), we find that

$$p_j(\psi) = \left|\sum_k C_k \int_R dx\phi_j^*(x)\phi_k(x)\right|^2 = \left|\sum_k C_k\delta_{jk}\right|^2 = |C_j|^2, \tag{1.50}$$

where Theorem 1.2 has been used and δ_{jk} is the Kronecker-delta symbol.[9] This means that the absolute square of each coefficient in Eq. (1.49) corresponds to the probability. Therefore, $\sum_k |C_k|^2 = 1$ because the sum of all probabilities have to become one.

For the case where some of the eigenvalues A_j's are the same, the orthogonality given by Theorem 1.2 is not always satisfied. However, even in this case, it is always possible to identify orthogonal $\phi_k(x)$'s with respect to which a unique linear combination given by Eq. (1.49) can be identified for any wavefunction $\psi(x)$. Then, each $|C_k|^2$ can be interpreted as the probability for the state to exist in the state represented by $\phi_k(x)$. Thus, for such a general state, although the results of measurement are not always certain, one can expect that the average over many repeated measurements, so called expectation value can always be calculated as described below.

Expectation Value

For a general normalized quantum state given by Eq. (1.49) the expectation value for the measurement of an operator $\hat{A}$ is given by

$$\langle\hat{A}\rangle_\psi = \sum_k p_k(\psi)A_k = \sum_k \left|\int_R dx\ \phi_k^*(x)\psi(x)\right|^2 A_k. \tag{1.51}$$

(continued)

[9] The Kronecker-delta symbol $\delta_{jk} = 1$ for $j = k$ and is zero otherwise.

Alternatively, the expectation value can be expressed as

$$\langle \hat{A} \rangle = \int_R dx\ \psi^*(x) \hat{A} \psi(x). \tag{1.52}$$

The equivalence of Eqs. (1.51) and (1.52) can be proved by using Eq. (1.49) and employing the orthogonality Theorem 1.2.

1.4 Quantum Particle in a One-Dimensional Box

Let us consider a particle with mass m contained in a one-dimensional box of length l. That is, the potential $V(x) = 0$ for $0 < x < l$, and $V(x) = \infty$ for $x \leq 0$ or $x \geq l$. Figure 1.3 illustrates the system and an example of a classical trajectory that bounces back and forth between two infinite walls at constant speed. The quantum mechanical behavior of this particle is drastically different, as will be shown in this section. The Hamiltonian operator within the box and the wavefunction outside the box are given by

$$\hat{H} = \frac{\hat{p}^2}{2m} \text{ for } 0 < x < l,$$
$$\psi(x, t) = 0 \text{ for } x \leq 0 \text{ or } x \geq l.$$

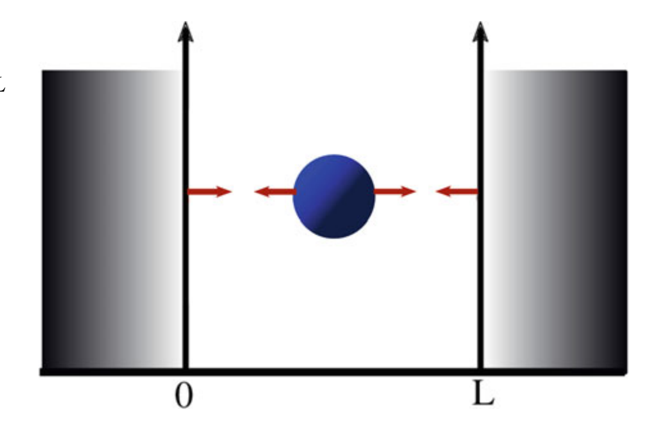


Fig. 1.3 One dimensional box, where the potential energy is zero for $0 < x < L$ and infinite outside of this region. The ordinate represents energy. The blue circle represents a classical particle, and the arrows represent the direction of their movement at different positions within the box

1.4.1 Time Independent Schrödinger Equation

Let us denote the eigenfunction with energy E as $\psi_E(x)$. Then, for $0 < x < l$,

$$\hat{H}\psi_E(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_E(x) = E\psi_E(x), \tag{1.53}$$

with the following boundary conditions: $\psi_E(0) = \psi_E(l) = 0$. A general solution for Eq. (1.53) is given by

$$\psi_E(x) = C_1 e^{ikx} + C_2 e^{-ikx}. \tag{1.54}$$

By plugging this into Eq. (1.53), one can show that

$$E = \frac{\hbar^2 k^2}{2m}. \tag{1.55}$$

However, this does not complete the solution yet because the boundary conditions need to be satisfied as well. Imposing the boundary conditions limits the possible values of k (therefore E). In other words, the wavefunction should become zero when $x = 0$ and $x = l$. Thus,

$$\psi_E(0) = C_1 + C_2 = 0, \tag{1.56}$$

from which we get $C_1 = -C_2$. Inserting this into Eq. (1.54) and imposing that $\psi(l) = 0$, we get

$$\psi_E(l) = C_1(e^{ikl} - e^{-ikl}) = 2iC_1 \sin(kl) = 0. \tag{1.57}$$

This condition is satisfied for nonzero C_1 only if $k = n\pi/l$ with $n = 1, 2, \ldots$. Inserting this into Eq. (1.55), we find that the energy is quantized as follows:

$$E_n = \frac{\pi^2\hbar^2 n^2}{2ml^2}, n = 1, 2, \ldots \tag{1.58}$$

Up to now, the constant C_1 has not been determined yet. Let us introduce a new constant $C = 2iC_1$ and label each eigenfunction with the integer quantum number n. Then,

$$\psi_n(x) = C \sin\left(\frac{n\pi x}{l}\right). \tag{1.59}$$

The normalization condition can be used to determine the constant C as follows:

$$1 = \int_0^l dx|\psi_n(x)|^2 = |C|^2 \int_0^l dx \ \sin^2\left(\frac{n\pi x}{l}\right)$$
$$= \frac{|C|^2}{2}\int_0^l dx\left(1 - \cos\left(\frac{2n\pi x}{l}\right)\right) = \frac{|C|^2 l}{2}. \tag{1.60}$$

Assuming that C is real and positive,[10] the above equation shows that $C = \sqrt{2/l}$. Therefore, the nth eigenfunction is given by

$$\psi_n(x) = \sqrt{\frac{2}{l}}\sin\left(\frac{n\pi x}{l}\right). \tag{1.61}$$

One can directly confirm that $\psi_n(x)$ given above satisfies the time independent Schrödinger equation, Eq. (1.53), for the energy given by Eq. (1.58).

It is clear that $\psi_n(x)$ given by Eq. (1.61) is not an eigenfunction of the position or momentum operator. On the other hand, it is an eigenfunction of $\hat{p}^2$ with an eigenvalue $\hbar^2\pi^2 n^2/l^2$. This is because the wavefunction is a combination of equal weight of those with positive and negative values of the same magnitude of the momentum, $\hbar\pi n/l$. This value of momentum indeed satisfies the de Broglie's relationship given that the wavelength $\lambda_n = 2l/n$ of $\psi_n(x)$ is used. Thus, the de Broglie wave is nothing but the Schrödinger's wavefunction.

The expectation value of position for $\psi_n(x)$ can be calculated as

$$\langle\hat{x}\rangle = \frac{2}{l}\int_0^l dx \sin\left(\frac{n\pi x}{l}\right) x \sin\left(\frac{n\pi x}{l}\right)$$
$$= \frac{2}{l}\int_0^l dx\left(\frac{1-\cos(2n\pi x/l)}{2}\right)x = \frac{l}{2}.$$

Thus, the average position is the center of the box and is independent of the quantum number n. On the other hand, the expectation value of momentum is always zero as follows:

$$\langle\hat{p}\rangle = \frac{2}{l}\frac{\hbar}{i}\int_0^l dx \sin\left(\frac{n\pi x}{l}\right)\frac{\partial}{\partial x}\sin\left(\frac{n\pi x}{l}\right)$$
$$= \frac{2}{l}\frac{\hbar}{i}\frac{n\pi}{l}\int_0^l dx \sin\left(\frac{n\pi x}{l}\right)\cos\left(\frac{n\pi x}{l}\right) = 0. \tag{1.62}$$

[10] C in fact can be a complex value with unit norm, which does not affect the outcome of any physical observable. Thus, this assumption is more of convenience rather than necessity.

In order to check the uncertainty relationship, let us also calculate the expectation values of $\hat{x}^2$ and $\hat{p}^2$. First, the expectation value of $\hat{x}^2$ is given by

$$\begin{aligned}
\langle \hat{x}^2 \rangle &= \frac{2}{l} \int_0^l dx \sin\left(\frac{n\pi x}{l}\right) x^2 \sin\left(\frac{n\pi x}{l}\right) \\
&= \frac{2}{l} \int_0^l dx \left(\frac{1 - \cos(2n\pi x/l)}{2}\right) x^2 \\
&= \frac{l^2}{3} + \frac{1}{n\pi} x \left(-\frac{l}{2n\pi}\right) \cos\left(\frac{2n\pi x}{l}\right)\Bigg|_0^l \\
&= \frac{l^2}{3} - \frac{l^2}{2n^2\pi^2}.
\end{aligned} \tag{1.63}$$

On the other hand, since $\psi_n(x)$ is an eigenfunction of $\hat{p}^2$, the expectation value is equal to the eigenvalue as follows:

$$\langle p^2 \rangle = 2mE_n = \frac{\hbar^2 n^2 \pi^2}{l^2}. \tag{1.64}$$

Therefore, the uncertainties of position and momentum are as follows:

$$\Delta x = \left(\langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2\right)^{1/2} = \left(\frac{l^2}{12} - \frac{l^2}{2n^2\pi^2}\right)^{1/2} = \frac{l}{2n\pi}\left(\frac{n^2\pi^2}{3} - 2\right)^{1/2}, \tag{1.65}$$

$$\Delta p = \left(\langle \hat{p}^2 \rangle - \langle \hat{p} \rangle^2\right)^{1/2} = \frac{\hbar n\pi}{l}. \tag{1.66}$$

The product of the above two uncertainties satisfies Heisenberg's uncertainty principle as follows:

$$\Delta x \Delta p = \frac{\hbar}{2}\left(\frac{n^2\pi^2}{3} - 2\right)^{1/2} \geq \frac{\hbar}{2}\left(\frac{\pi^2}{3} - 2\right)^{1/2} > \frac{\hbar}{2}. \tag{1.67}$$

1.4.2 Time Dependent States

For each eigenfunction, one can define the following time dependent stationary wavefunction.

$$\psi_n(x, t) = \psi_n(x) e^{-iE_n t/\hbar} = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right) e^{-iE_n t/\hbar}, \tag{1.68}$$

where E_n is given by Eq. (1.58). This satisfies the time dependent Schrödinger equation as shown below.

$$i\hbar\frac{\partial}{\partial t}\psi_n(x,t) = E_n\psi_n(x,t) = \hat{H}\psi_n(x,t). \tag{1.69}$$

Now let us consider the following linear combination:

$$\psi(x,t) = \sum_{n=1}^{\infty} C_n\psi_n(x,t) = \sum_{n=1}^{\infty} C_n\sqrt{\frac{2}{l}}\sin\left(\frac{n\pi x}{l}\right)e^{-iE_nt/\hbar}. \tag{1.70}$$

Then, one can show that

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\psi(x,t) &= \sum_{n=1}^{\infty} C_n i\hbar\frac{\partial}{\partial t}\psi_n(x,t) \\ &= \sum_{n=1}^{\infty} C_n E_n\psi_n(x,t) = \sum_{n=1}^{\infty} C_n\hat{H}\psi_n(x,t) = \hat{H}\psi(x,t), \end{aligned} \tag{1.71}$$

where the last equality holds because $\hat{H}$ is a linear operator.

Equation (1.71) proves that any linear combination of the eigenstates with appropriate time dependent factor $e^{-iE_nt/\hbar}$ satisfies the time dependent Schrödinger equation. Although we have specifically assumed that $\psi_n(x)$ is the solution of the time independent Schrödinger equation for a quantum particle in a box, Eq. (1.71) is generally true for any Hamiltonian.

1.4.3 Completeness

The eigenfunctions of the Hamiltonian form a *complete orthonormal basis set* for all quadratically integrable functions defined for $0 < x < l$. The meaning of this will be explained in more detail below. First, orthonormality[11] can be shown explicitly as

$$\begin{aligned} \int_0^{\infty}\psi_n^*(x)\psi_m(x)dx &= \frac{2}{l}\int_0^l \sin\left(\frac{\pi nx}{l}\right)\sin\left(\frac{\pi mx}{l}\right)dx \\ &= \frac{1}{l}\int_0^l\left\{\cos\left(\frac{\pi(n-m)x}{l}\right) - \cos\left(\frac{\pi(n+m)x}{l}\right)\right\} = \delta_{nm}, \end{aligned} \tag{1.72}$$

[11] This means being orthogonal and normalized.

where δ_{nm} is the Kronecker-delta symbol introduced in Eq. (1.50). The set of eigenfunctions form a complete basis in the sense that any well-behaved function can be expressed as

$$f(x) = \sum_{m=1}^{\infty} C_m \psi_m(x), \tag{1.73}$$

where C_n is uniquely determined by the following relation:

$$\int_0^l \psi_n^*(x) f(x) dx = \sum_{m=1}^{\infty} C_m \int_0^l \psi_n^*(x) \psi_m(x) dx = \sum_{m=1}^{\infty} C_m \delta_{nm} = C_n. \tag{1.74}$$

Inserting the above relation into Eq. (1.73),

$$f(x) = \sum_{m=1}^{\infty} \psi_m(x) \int_0^l \psi_m^*(x') f(x') dx' = \int_0^l \sum_{m=1}^{\infty} \psi_m(x) \psi_m^*(x') f(x') dx'. \tag{1.75}$$

Because the above relation holds for any function $f(x)$, we come up with the following identity:

$$\sum_{m=1}^{\infty} \psi_m(x) \psi_m^*(x') = \delta(x - x'), \tag{1.76}$$

where $\delta(x - x')$ is called Dirac-delta function, a singular "function" that is in fact something called a "distribution" mathematically. More detailed description of this is provided in Appendix.

Equation (1.76) is an example of the completeness relationship. Although this was demonstrated here for the particular example of the particle in a box, it is in fact possible to identify a set of eigenfunctions satisfying such an identity for any Hamiltonian. Such eigenfunctions form a complete basis set.

1.5 Summary and Questions

The theory of quantum mechanics is based on two principles well established through classical mechanics. These are fundamental principles that (i) the energy of a closed isolated system remains conserved (the principle of energy conservation), and that (ii) any physical processes are manifestations of clear relationships between certain causes and effects that are both well defined and quantifiable (the principle of causality).

However, the theory of quantum mechanics is a complete departure from that of classical mechanics in that simultaneous determination of position and momentum of any physical object cannot be made with arbitrary precision. Rather, the precision of one or the other has to be given up according to the uncertainty principle, as shown by Eq. (1.19) for the case of one dimensional position and momentum.

Within the formalism of quantum mechanics, the classical notion that position and momentum can be determine completely and simultaneously is an approximation that appears to be valid only when the action, another well-established concept in classical mechanics implying "the outcome of applying force for certain time," is much larger than $\hbar$, the reduced Planck constant. This posed serious problem both conceptually and practically because it meant that classical Newton's equation or classical Hamiltonian dynamics (a more general form of classical dynamics) can no longer be used as rules to describe the dynamics or to understand the relationship of causality.

The notion of the "dual nature of wave and particle," as first expressed by de Broglie for simple cases, Eq. (1.18), and articulated by Bohr, provided new conceptual basis for understanding the uncertainty principle and motivated further experimental discoveries. Then, the formulations by Schrödinger and Heisenberg made it possible to describe states and dynamics of quantum particles while not violating the two fundamental principles of energy conservation and causality, as stated by (i) and (ii) above.

The success of Schrödinger equation, Eq. (1.27), and its time independent version for stationary states, Eq. (1.34), led to the establishment of the theory of quantum mechanics as an ultimate theory for all atomic and molecular properties and phenomena. Although there have been and are still fundamental debates about the physical meaning of the Schrödinger equation, the fact that actual states of a system and physically measured quantities have to be considered separately is now well established.

While the Schrödinger equation appears to provide a full description of a quantum mechanical state, what is being described by the equation, namely a wavefunction, cannot in fact be measured experimentally. Rather, a wavefunction can provide only the probability of certain outcomes of the measurements in general. The exception to this is when the state is in an eigenstate of the operator corresponding to measurement, which often involves the measurement process itself as ways to prepare such states. In this case, the outcome of the measurement is certain and it is assumed that the complete information on the state of the system can be deduced once we are able to determine the eigenstates of all other compatible physical observables.

Another difficulty of quantum mechanics as a theory lies in the fact that the solution of the Schrödinger equation is difficult to get exactly except for very simple model systems. As yet, detailed study of such few examples, for which exact solutions are available, helps understand clearly major concepts and phenomena that are unique for quantum mechanics. These include superposition states as linear combinations of other states and important rules concerning definitions and interpretations of measurements. A short overview of the problem of quantum particle in a one dimensional box, described in Sect. 1.4, serves as a good example.

Questions

- Can blackbody radiation and the photoelectric effect be explained only if the energy of light is proportional to its frequency?
- Is it possible for both the position of a quantum particle and momentum along the same direction to be determined with arbitrary precision?
- What happens to the de Broglie wave if a particle completely stops?
- Given that the dynamics of a closed classical system is energy conserving, is the dynamics of the corresponding closed quantum system also energy conserving?
- For any quantum system, does full information on its wavefunction allow calculation of the outcome of any physical observable?
- Is it possible for the eigenvalue of a Hermitian operator to become a complex number?
- What happens if a quantum mechanical operator is not linear?
- What is the relationship between time dependent and time independent Schrödinger equations?

Appendix: Dirac-Delta Function

Dirac-delta function [23] is defined by the following two properties:

$$\delta(x - x') = 0 \text{ for } x \neq x', \tag{1.77}$$

$$\int_{-\infty}^{\infty} dx f(x)\delta(x - x') = f(x'), \tag{1.78}$$

where $f(x)$ is an arbitrary continuous and integrable function. In fact, the Dirac-delta function is not a genuine function, but a limit of a series of functions, which is known as distribution in mathematics. Thus, more rigorously, the Dirac-delta function is defined as follows:

$$\delta(x) = \lim_{\epsilon \to 0} \delta^{(\epsilon)}(x), \tag{1.79}$$

where $\delta^{(\epsilon)}(x)$ is a well-defined function for finite ϵ but becomes singular in the limit of $\epsilon = 0$. There is no unique way to define the sequence of $\delta^{(\epsilon)}(x)$. Well-known forms of $\delta^{(\epsilon)}(x)$ are as follows.

$$\delta_h^{(\epsilon)}(x) = \begin{cases} 1/\epsilon, & -\epsilon/2 < x < \epsilon/2 \\ 0, & |x| > \epsilon/2 \end{cases}, \tag{1.80}$$

$$\delta_e^{(\epsilon)}(x) = \frac{1}{2\epsilon} e^{-|x|/\epsilon}, \tag{1.81}$$

$$\delta_l^{(\epsilon)}(x) = \frac{1}{\pi} \frac{\epsilon}{x^2 + \epsilon^2}, \tag{1.82}$$

$$\delta_g^{(\epsilon)}(x) = \frac{1}{\epsilon\sqrt{\pi}} e^{-x^2/\epsilon^2}, \tag{1.83}$$

$$\delta_s^{(\epsilon)}(x) = \frac{1}{\pi} \frac{\sin(x/\epsilon)}{x} = \frac{1}{2\pi} \int_{-1/\epsilon}^{1/\epsilon} e^{ikx} dk. \tag{1.84}$$

In the above equations, different subscripts denote different ways to define the sequence such as "hard step function," "exponential function," "Lorentzian function," "Gaussian function," and "sine function." Note that the second equality in Eq. (1.84) can be shown by direct integration of the last expression. One of the most frequently used form of Dirac-delta function in quantum mechanics employs Eq. (1.84). When this is inserted into Eq. (1.79), the resulting Dirac-delta function becomes

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx} dk. \tag{1.85}$$

Exercise Problems with Solutions

1.1 How many photons per second are generated in a 100.0 watt beam of red light with 700.0 nm wavelength?

Solution 1.1 The 100.0 watt beam of light corresponds to $E_{light} = 100.0$ J per second. According to Eqs. (1.14) and (1.12), this corresponds to the following number of photons per second:

$$n = \frac{100.0}{6.626 \times 10^{-34}} \frac{7.000 \times 10^{-7}}{2.998 \times 10^8} = 3.523 \times 10^{20}.$$

1.2 Light is incident on a metal with work function 1 eV (1.602×10^{-19} J), which causes ejection of electrons with 1.00 nm de Broglie wavelength. Assuming that the magnitude of the momentum of electron is given by $m_e v_e$, where m_e and v_e are the mass and speed of electron, determine the frequency of the incident light?

Solution 1.2 According to Eq. (1.18) and the assumption that $p_e = m_e v$, the speed of the electron is given by

$$v_e = \frac{h}{\lambda_{dB} m_e} = \frac{6.626 \times 10^{-34} \mathrm{kgm^2s^{-1}}}{(1.00 \times 10^{-9}\mathrm{m}) \times (9.109 \times 10^{-31}\mathrm{kg})}.$$

Using the above value in Eq. (1.15), we find that the frequency of incident light is given by

$$\nu = \frac{\Phi}{h} + \frac{m_e}{2h} v_e^2 = 6.055 \times 10^{14} \mathrm{s}^{-1}.$$

1.3 A particle with mass 1 g is placed on a sharp tip of 1.00 mm width. The particle falls off the tip if it goes outside of its width. According to the Heisenberg's uncertainty principle, what is the maximum time the particle can stay on top of the tip?

Solution 1.3 For the particle to stay on top of the tip, the uncertainty of position has to be equal to or less than 1 mm. According to the Heisenberg's uncertainty relation, Eq. (1.19), this implies that

$$\Delta p \geq \frac{\hbar}{\Delta x} = \frac{6.626 \times 10^{-34}\ \mathrm{kgm^2s^{-1}}}{4 \times 3.14 \times 1.00 \times 10^{-3}\mathrm{m}} = 5.28 \times 10^{-32}\ \mathrm{kg \cdot m \cdot s^{-1}}.$$

If the particle stays on top of the tip for Δt, this means that the magnitude of the momentum is approximately given by $m\Delta x/\Delta t$. Since $p > \Delta p$, this means that

$$\begin{aligned}\Delta t &\approx \frac{m\Delta x}{p} \leq \frac{m\Delta x}{\Delta p} \\ &\leq \frac{(1.00 \times 10^{-3}\ \mathrm{kg}) \times (1.00 \times 10^{-3}\ \mathrm{m})}{5.26 \times 10^{-32}\ \mathrm{kg \cdot m} \cdot s^{-1}} = 1.89 \times 10^{25}\ \mathrm{s}.\end{aligned}$$

1.4 A proton is confined in a one dimensional box of 0.2 nm length. Use the uncertainty principle to determine its minimum kinetic energy.

Solution 1.4 The minimum uncertainty in the momentum of the proton with the uncertainty in position of 2 Å, according to Eq. (1.19), is given by

$$\Delta p = \frac{\hbar}{2\Delta x} = 2.64 \times 10^{-25} \mathrm{kg \cdot ms^{-1}}.$$

For the above minimum uncertainty in momentum, the minimum kinetic energy is given by

$$E_{min} = \frac{1}{2}\frac{\Delta p^2}{m} = 2.08 \times 10^{-23}\ \mathrm{J}.$$

1.5 The wavefunction of a particle in one dimension is given by

$$\psi(x) = Ne^{-x^2/2}.$$

Determine the normalization constant N. Prove that Heisenberg's uncertainty principle is satisfied for this wavefunction.

Solution 1.5 For the wavefunction to be normalized,

$$1 = \int_{-\infty}^{\infty} dx |\psi(x)|^2 = N^2 \int_{-\infty}^{\infty} dx e^{-x^2} = N^2 \sqrt{\pi}.$$

Therefore, $N = 1/\pi^{1/4}$. With this normalization constant, it is straightforward to calculate the expectation values of position, position square, momentum, and momentum square as follows:

$$\begin{aligned}
\langle \hat{x} \rangle &= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx x e^{-x^2} = 0, \\
\langle \hat{x}^2 \rangle &= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx x^2 e^{-x^2} \\
&= \frac{1}{\sqrt{\pi}} \left[-\frac{1}{2} x e^{-x^2} \Big|_{-\infty}^{\infty} + \frac{1}{2} \int_{-\infty}^{\infty} dx e^{-x^2} \right] \\
&= \frac{1}{\sqrt{\pi}} \frac{1}{2} \sqrt{\pi} = \frac{1}{2},
\end{aligned}$$

$$\begin{aligned}
\langle \hat{p} \rangle &= \frac{1}{\sqrt{\pi}} \frac{\hbar}{i} \int_{-\infty}^{\infty} dx e^{-x^2/2} \frac{d}{dx} e^{-x^2/2} = \frac{1}{\sqrt{\pi}} \frac{\hbar}{i} \int_{-\infty}^{\infty} dx e^{-x^2/2} x e^{-x^2/2} = 0, \\
\langle \hat{p}^2 \rangle &= -\frac{1}{\sqrt{\pi}} \hbar^2 \int_{-\infty}^{\infty} dx e^{-x^2/2} \frac{d^2}{dx^2} e^{-x^2/2} \\
&= -\frac{\hbar^2}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx \left(-e^{-x^2} + x^2 e^{-x^2} \right) \\
&= -\frac{\hbar^2}{\sqrt{\pi}} \left[-\sqrt{\pi} + \frac{1}{2} \sqrt{\pi} \right] = \frac{\hbar^2}{2}.
\end{aligned}$$

Employing the above results, we can calculate the uncertainties of position and momentum as follows:

$$\begin{aligned}
\Delta x &= \sqrt{\langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2} = \frac{1}{\sqrt{2}}, \\
\Delta p &= \sqrt{\langle \hat{p}^2 \rangle - \langle \hat{p} \rangle^2} = \frac{\hbar}{\sqrt{2}}.
\end{aligned}$$

The above results show that $\Delta x \Delta p = \hbar/2$. Thus, the given wavefunction is a minimum uncertainty state.

1.6 An operator $\hat{O}$ is defined by the following action on a given function $f(x)$.

$$\hat{O} f(x) = f(x)^2.$$

Prove that this operator is not linear.

Solution 1.6 Given that $f(x) = C_1 f_1(x) + C_2 f_2(x)$,

$$\begin{aligned}\hat{O}(C_1 f_1(x) + C_2 f_2(x)) &= (C_1 f_1(x) + C_2 f_2(x))^2 \\ &= C_1^2 f_1(x)^2 + 2C_1 C_2 f_1(x) f_2(x) + C_2 f_2(x)^2.\end{aligned}$$

This is not in general equal to $C_1 \hat{O} f_1(x) + C_2 \hat{O} f_2(x) = C_1 f_1(x)^2 + C_2 f_2(x)^2$. Therefore, the given operator is not linear.

1.7 An operator $\hat{O}$ is defined by the following action on a given function $f(x)$.

$$\hat{O} f(x) = \frac{d}{dx} x f(x).$$

Prove that this operator is linear.

Solution 1.7 Given that $f(x) = C_1 f_1(x) + C_2 f_2(x)$,

$$\begin{aligned}\hat{O}(C_1 f_1(x) + C_2 f_2(x)) &= \frac{d}{dx} x\,(C_1 f_1(x) + C_2 f_2(x)) \\ &= C_1 \frac{d}{dx} x f_1(x) + C_2 \frac{d}{dx} x f_2(x) \\ &= C_1 \hat{O} f_1(x) + C_2 \hat{O} f_2(x).\end{aligned}$$

Therefore, the given operator is linear.

1.8 Use the particle in a box problem, where the wavefunction is zero outside the region of $0 < x < l$, to prove that momentum operator is Hermitian. Hint: You need to use integration by part.

Solution 1.8 For arbitrary wavefunctions $\psi(x)$ and $\phi(x)$ for the particle in a box of length l, integration by part results in the following identity:

$$\int_0^l dx \phi^*(x) \frac{\hbar}{i} \frac{\partial}{\partial x} \psi(x) = \frac{\hbar}{i} \phi^*(x) \psi(x) \Big|_0^l - \frac{\hbar}{i} \int_0^l dx \left(\frac{\partial \phi^*(x)}{\partial x} \right) \psi(x).$$

Since $\psi(x)$ and $\phi(x)$ are zero for $x = 0, l$, the first on the righthand side of the above equation vanishes. Therefore,

$$\int_0^l dx \phi^*(x) \frac{\hbar}{i} \frac{\partial}{\partial x} \psi(x) = \left(\int_0^l dx \psi^*(x) \frac{\hbar}{i} \frac{\partial}{\partial x} \phi(x) \right)^* .$$

This proves that the momentum operator is Hermitian.

1.9 Consider a particle in a box of unit length ($l = 1$) with the following wavefunction:

$$\psi(x) = \sin(\pi x) + \sin(2\pi x).$$

If energy is measured for this particle, what are possible values of the measurement and their respective probabilities? What is the probability for this particle to be found in the region of $0 < x < 1/4$?

Solution 1.9 For a particle in a box of unit length, the normalized eigenfunctions are

$$\phi_n(x) = \sqrt{2}\sin(n\pi x),\ \ n = 1, 2, 3, \ldots \tag{1.86}$$

for which the eigenvalue of the Hamiltonian, $E_n = \hbar^2\pi^2 n^2/(2m)$. Therefore, the given function can be expressed as

$$\psi(x) = \frac{1}{\sqrt{2}}\phi_1(x) + \frac{1}{\sqrt{2}}\phi_2(x).$$

This expression implies that possible values of the measurement of energy are $E_1 = \hbar^2\pi^2/(2m)$ and $E_2 = 4\hbar^2\pi^2/(2m)$, both with probability $1/2$. The probability for the particle to be in the region between 0 and $1/4$ can be calculated as follows:

$$\begin{aligned}
Pr[0 < x < 1/4] &= \int_0^{1/4} |\psi(x)|^2 dx \\
&= \int_0^{1/4} \left(\sin^2(\pi x) + 2\sin(\pi x)\sin(2\pi x) + \sin^2(2\pi x)\right) dx \\
&= \int_0^{1/4} \left(\frac{1}{2}(1 - \cos(2\pi x)) + \cos(\pi x) - \cos(3\pi x)\right. \\
&\qquad \left. + \frac{1}{2}(1 - \cos(4\pi x))\right) dx \\
&= \left[x - \frac{1}{4\pi}\sin(2\pi x) + \frac{1}{\pi}\sin(\pi x) - \frac{1}{3\pi}\sin(3\pi x)\right. \\
&\qquad \left. - \frac{1}{8\pi}\sin(4\pi x)\right]_0^{1/4} = 0.32.
\end{aligned}$$

1.10 A quantum particle with unit mass ($m = 1$) is confined in a box of length $l = 2$, and is in a state represented by the following wavefunction: $\psi(x) = N(\sin(\pi x) + \sin(2\pi x))$, where N is a normalization constant. Determine N and calculate the expectation value of the energy.

Solution 1.10 The normalized eigenfunction and eigenvalue are respectively,

$$\phi_n(x) = \sin(\frac{n\pi x}{2}),\ \ E_n = \frac{\hbar^2\pi^2 n^2}{8},$$

where $n = 1, 2, \cdots$. Therefore,

$$\psi(x) = N(\phi_2(x) + \phi_4(x)).$$

It is clear or possible to show by direct integration that $2N^2 = 1$. As a result, $N = 1/\sqrt{2}$. Either by direct integration or using the above expression for $\psi(x)$, we find that

$$\langle E\rangle = \frac{1}{2}E_2 + \frac{1}{2}E_4 = \frac{\hbar^2\pi^2}{4} + \hbar^2\pi^2 = \frac{5}{4}\hbar^2\pi^2.$$

1.11 Consider a particle in a box with $l = 2$. Assume that the wavefunction at $t = 0$ is given by $\psi(x)$ in **Problem 1.9**. Then, what is the wavefunction at time $t = 1$?

Solution 1.11 For particle in a box of length $l = 2$, the eigenfunctions of the Hamiltonian are

$$\phi_n(x) = \sin\left(\frac{n\pi x}{2}\right), n = 1, 2, \ldots$$

for which the eigenvalue $E_n = \hbar^2\pi^2 n^2/(8m)$. Thus, the given $\psi(x)$ can be expressed as follows:

$$\psi(x) = \phi_2(x) + \phi_4(x).$$

For the above wavefunction as that for $\psi(x, t = 0)$, the wavefunction at arbitrary time is then given by

$$\begin{aligned}\psi(x,t) &= e^{-iE_2t/\hbar}\phi_2(x) + e^{-iE_4t/\hbar}\phi_4(x)\\ &= e^{-i\hbar\pi^2t/(2m)}\phi_2(x) + e^{-i2\hbar\pi^2t/m}\phi_4(x).\end{aligned}$$

Problems

1.12 Calculate de Broglie wavelength for each case described below.

(a) An electron moving at the speed of 10^6 m/s.
(b) A proton moving at the speed of 10^5 m/s.
(c) An oxygen molecule moving at the speed of 300 m/s.
(d) A human body of mass 70 kg moving at the speed of 10 m/s.

1.13 Prove that Eqs. (1.51) and (1.52) for the expectation value are equivalent.

1.14 Use the example of particle in a box problem to prove that the following operator is Hermitian:

$$\hat{A} = \frac{1}{2}\left(\hat{x}\hat{p} + \hat{p}\hat{x}\right).$$

1.15 Consider a particle of unit mass ($m = 1$) in a box of unit length ($l = 1$) with the following wavefunction:

$$\psi(x) = N(\sin(\pi x) - 2\sin(2\pi x) + \sin(3\pi x)).$$

(a) Determine the normalization constant N so that the wavefunction $\psi(x)$ is normalized.
(b) Determine the expectation value of the energy for this particle.
(c) If the energy is measured for this particle, what are actual values of the individual measurement possible and their respective probabilities?
(d) Given that the wavefunction above is $\psi(x, t = 0)$, determine the smallest time $t > 0$ for which $\psi(x, t) = \psi(x)$.

1.16 For a particle with unit mass ($m = 1$) confined in a box of unit length $l = 1$, its wavefunction is given by $\psi(x) = 4Nx$ for $0 < x \le 1/4$, N for $1/4 < x < 3/4$, and $4N(1 - x)$ for $3/4 \le x < 1$. Answer the following questions.

(a) Determine N so that the wavefunction is normalized.
(b) Determine the expectation value of the energy for this particle.
(c) Calculate the probability for the particle to have energy $\hbar^2\pi^2/2$.
(d) Calculate the probability for the particle to have energy $2\hbar^2\pi^2$.
(e) Calculate the uncertainty in the position of the particle. What is the expected minimum of the uncertainty in the momentum of this particle?

Chapter 2
Dirac Notation and Principles of Quantum Mechanics



The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, ...

— Paul A. M. Dirac

Abstract This chapter introduces Dirac's notations for kets and bras, which represent quantum states, and the rules for inner and outer products between them. Operators are defined as linear combinations of outer products between kets and bras. The definition of a Hermitian operator in this Dirac notation and proofs of its properties are provided. Based on expressions for position, momentum, and Hamiltonian operators, time dependent and time independent Schrödinger equations are also provided. After important identities concerning commutators and unitary operators are detailed, the results for particle in a box problem are re-expressed in the Dirac notation. The chapter concludes with introduction of direct products that are used to expand the dimension of the state space.

2.1 Formulation of Quantum Mechanics

Schrödinger's formulation of quantum mechanics, as introduced in Chap. 1, is based on the assumption that quantum states can be represented by *complex functions of position* and that all physical observables can be expressed as *operators acting on the wavefunction through the position variable*. Schrödinger's formulation has been essential in obtaining practical solutions of quantum mechanical problems. However, because it gives the position a special role, the distinctions between position as a variable for describing quantum state, as an operator for position measurement, and as an outcome of the measurement, are not always expressed clearly. This can sometimes cause confusion and misunderstanding.

On the other hand, within Heisenberg's formulation of quantum mechanics, which in fact preceded Schrödinger's formulation by a few months, states and operators are represented as vectors and matrices, and position and momentum

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operators are treated in more equivalent manner. Another major difference of Heisenberg's formulation is that what changes with time are operators themselves, rather than the state of a quantum system as assumed in Schrödinger's formulation. Heisenberg's formulation makes the role of an operator clear. It is also convenient if the eigenstates and eigenvalues are known or can be determined by other means. However, dealing with all the matrix and vector elements often can be cumbersome if the number of states is large or infinite.

Although the two formulations by Schrödinger and Heisenberg appear to be completely different, they can in fact be related to each other through an appropriate transformation from the function space to the vector space. Dirac facilitated clarification of this relationship by inventing an elegant set of notations and rules, which make such transformations look very natural.[1] The efficacy of the Dirac notations in exposing the major principles of quantum mechanics has made it the most popular framework for describing quantum mechanics.

This chapter provides a concise description of the Dirac notation and presents the principles of quantum mechanics embedded in that notation [5, 6, 8]. The approach here is somewhat axiomatic in the sense that abstract mathematical definitions are given first without offering clear physical justifications. However, once a reader becomes familiar with them, understanding quantum mechanical principles will be much more straightforward.

2.2 Ket, Bra, and Products

It is important to note that the state of a quantum system in Schrödinger's formulation is represented by the entirety of the wavefunction, not by its particular value at certain position as the notation $\psi(x)$ may suggest. Likewise, a quantum mechanical operator should be viewed as the entire mapping from one state (the full set of values of wavefunction at all positions) to another state. Thus, $\hat{A}(\hat{x})\psi(x)$ in Schrödinger's formulation should be viewed as representing the *full set of results* of "multiplying the value of function $A(x)$ with the value of the wavefunction at the same position x."

A quantum mechanical state, even when represented by Schrödinger's wavefunction, can be viewed as a complex-valued vector in Hilbert space [24], with each element of this vector representing the value of the wavefunction at specific position. Once this notion of a vector in abstract function space is accepted, its components can be transformed to different ones involving parameters other than position variable through an appropriate transformation. In this sense, one can perceive a quantum state as a vector in abstract function space, which exists independent of how it is represented. Dirac represented such a vector by a **ket** or a **bra** equivalently.

[1] Mathematically speaking, Dirac notation can simply be considered as an effective visualization tool to introduce a complete and normed (or inner product) complex vector space, so called Hilbert space, and mappings defined in the Hilbert space.

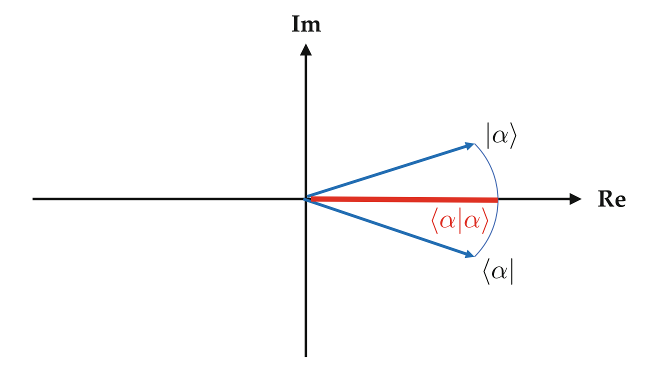


Fig. 2.1 A simple illustration of the relationship between a ket $|\alpha\rangle$, its Hermitian adjoin, bra $\langle\alpha|$, and the corresponding norm, $\langle\alpha|\alpha\rangle$, which corresponds to the projection on to the positive side of the real axis

The relationship between a ket and its corresponding bra is like a complex number and its conjugate (see Fig. 2.1). More detailed description is provided below.

Notation and Properties of Ket and Ket Space

A ket is denoted as $|\cdots\rangle$, where $\cdots$ represents the parameters specifying the ket, and has the following properties.

- Given two quantum mechanical states respectively represented by $|\alpha\rangle$ and $|\beta\rangle$ defined in the same vector space, it is possible to construct a different ket as their linear combinations as follows:

$$|\gamma\rangle = c_1|\alpha\rangle + c_2|\beta\rangle, \tag{2.1}$$

  where c_1 and c_2 are arbitrary complex numbers. This linear combination, indeed, represents a different quantum mechanical state as long as $|\alpha\rangle$ and $|\beta\rangle$ are independent, which means that the two are not related to each other by a constant factor.
- Any two kets related by a constant factor is viewed as representing the same state. In other words, one of the major assumptions of quantum mechanics is that *multiplying a ket with a nonzero complex number does not alter the physical state*. That is, $|\alpha\rangle$ and $c|\alpha\rangle$ (with $c \neq 0$) represent the same quantum state.[2] For this reason, only the relative value of c_1 to c_2 does matter in Eq. (2.1).
- A complete set of all the kets that can be constructed through linear combinations constitute an abstract vector space called **ket space**.

[2]Multiplication of any ket or bra with zero results in the null ket or bra.

A bra space is a vector space *dual* to a **ket space**. Mathematically, these two can define an **inner product space** as will be shown below. Using the terms of matrix theory, a ket can be viewed as a column vector of complex numbers, and bra as its complex conjugate and transpose, thus a row vector consisting of complex conjugates. For every ket $|\alpha\rangle$, there exists a unique bra denoted as $\langle\alpha|$ and vice versa. Given a ket defined as a linear combination of different kets, the corresponding bra can be obtained according to the following rule.

Relationship Between Ket and Bra Space

A state expressed as a linear combination of kets in a ket space is equivalent to the same linear combination of bras in the corresponding bra space but with complex conjugates of the corresponding coefficients as follows.

$$c_1|\alpha\rangle + c_2|\beta\rangle + \cdots \Leftrightarrow \langle\alpha|c_1^* + \langle\beta|c_2^* + \cdots . \tag{2.2}$$

Between a bra and a ket, two types of products can be defined. One is the **inner product**, and the other is the **outer product**. The **inner product** is defined only between *a ket on the right hand side* and *a bra on the left hand side*. More detailed definitions and properties are provided below.

Definition and Properties of Inner Product

The inner product between a ket $|\alpha\rangle$ and a bra $\langle\beta|$ results in a complex number, and is expressed as

$$(\langle\beta|) \cdot (|\alpha\rangle) = \langle\beta|\alpha\rangle, \tag{2.3}$$

where $\cdot$ is a temporary symbol used to denote the product. There are three important properties involving inner products.

- Two states represented by $|\alpha\rangle$ and $|\beta\rangle$ are called orthogonal to each other if $\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$.
- The complex conjugate of an inner product is equal to the inner product between corresponding ket and bra interchanged as follows:

$$\langle\beta|\alpha\rangle = \langle\alpha|\beta\rangle^*, \tag{2.4}$$

where * represents the complex conjugate. As a result, $\langle\alpha|\alpha\rangle$ is always real.

(continued)

- The inner product between a ket and bra of the same state is nonnegative. Namely,

$$\langle\alpha|\alpha\rangle \geq 0. \tag{2.5}$$

The equality above holds true only when $|\alpha\rangle$ is a null ket that represents a non-existent state. The inner product $\langle\alpha|\alpha\rangle$ serves as the measure of the size of the ket (or bra), and its square root is called *norm*. A *normalized state* has a unit norm. As an outcome of Eq. (2.5), the magnitude of the inner product between two normalized states is always less than or equal to one (see Appendix of this chapter).

The **outer product** is defined only between *a ket on the left hand side* and *a bra on the right hand side*, and is used to represent a mapping from a ket (bra) to a bra (ket). Its notation and detailed properties are provided below.

Definition and Properties of Outer Product

The outer product between a ket $|\alpha\rangle$ and a bra $\langle\beta|$ is defined as

$$(|\alpha\rangle)\cdot(\langle\beta|) = |\alpha\rangle\langle\beta|, \tag{2.6}$$

where again $\cdot$ is a temporary symbol used to denote the product. In relation to inner products, outer products have two important properties as described below.

- The combination of inner and outer products satisfy the following *associative rule*:

$$(|\alpha\rangle\langle\beta|)\cdot|\gamma\rangle = |\alpha\rangle\cdot(\langle\beta|\gamma\rangle) = |\alpha\rangle\langle\beta|\gamma\rangle. \tag{2.7}$$

That is, $|\alpha\rangle\langle\beta|$ is nothing but an **operator** that turns an arbitrary state $|\gamma\rangle$ into $|\alpha\rangle$ multiplied with a complex number $\langle\beta|\gamma\rangle$. Similarly, the following associative rule always applies:

$$(\langle\alpha|\beta\rangle)\,\langle\gamma| = \langle\alpha|\,(|\beta\rangle\langle\gamma|) = \langle\alpha|\beta\rangle\langle\gamma|, \tag{2.8}$$

which shows that $|\beta\rangle\langle\gamma|$ is an operator that turns an arbitrary bra state $\langle\alpha|$ into another bra state $\langle\gamma|$ multiplied with a complex number $\langle\alpha|\beta\rangle$.

(continued)

- Both inner and outer products satisfy distributive rules as follows.

$$\langle\alpha|\left(C_1|\beta\rangle + C_2|\gamma\rangle\right) = C_1\langle\alpha|\beta\rangle + C_2\langle\alpha|\gamma\rangle, \tag{2.9}$$

$$\left(C_1|\beta\rangle + C_2|\gamma\rangle\right)\langle\alpha| = C_1|\beta\rangle\langle\alpha| + C_2|\gamma\rangle\langle\alpha|. \tag{2.10}$$

2.3 Operators

An operator acts on a ket (bra) and produces another ket (bra). It can always be represented as a linear combination of outer products of kets and bras. Like the relationship between ket and bra, for a given operator $\hat{O}$, there is an equivalent form of the same operator that "mirrors" the action in ket space to the one in bra space, and vice versa as describe below.

Hermitian Conjugate of an Operator

Given an operator $\hat{O}$, its **Hermitian conjugate** $\hat{O}^\dagger$ satisfies the following dual correspondence rule for an arbitrary ket $|\alpha\rangle$:

$$\hat{O}|\alpha\rangle \Leftrightarrow \langle\alpha|\hat{O}^\dagger. \tag{2.11}$$

Therefore, if $\hat{O} = c_1|\alpha_1\rangle\langle\beta_1| + c_2|\alpha_2\rangle\langle\beta_2| + \cdots$,

$$\hat{O}^\dagger = c_1^*|\beta_1\rangle\langle\alpha_1| + c_2^*|\beta_2\rangle\langle\alpha_2| + \cdots . \tag{2.12}$$

For arbitrary $|\alpha\rangle$ and $|\beta\rangle$, one can show that

$$\langle\alpha|\hat{O}^\dagger|\beta\rangle = \left(\langle\beta|\hat{O}|\alpha\rangle\right)^* . \tag{2.13}$$

For a given operator $\hat{O}$, its **eigenket**[3] is defined as the ket satisfying the following relationship:

$$\hat{O}|u\rangle = \lambda_u|u\rangle, \tag{2.14}$$

where λ_u is the **eigenvalue** of the operator $\hat{O}$ corresponding to the eigenket $|u\rangle$ and is a complex number in general. According to the definition of the Hermitian

[3] The state represented by this eigenket is called **eigenstate**.

conjugate, Eq. (2.14) implies that

$$\langle u|\hat{O}^{\dagger} = \langle u|\lambda_u^* = \lambda_u^* \langle u|, \tag{2.15}$$

where λ_u^* is the complex conjugate of λ_u.

The operator that does not alter any ket or bra is called the identity operator, and is denoted as $\hat{1}$. That is, any ket or bra is an eigenket or eigenbra of the identity operator with its eigenvalue as one.

2.3.1 Hermitian Operator

Definition of Hermitian Operator

An operator $\hat{A}$ is **Hermitian** if it is identical to its own Hermitian conjugate as follows:

$$\hat{A} = \hat{A}^{\dagger}. \tag{2.16}$$

Therefore, inserting the above identity into Eq. (2.13), one can show that the Hermitian operator $\hat{A}$ satisfies the following identity:

$$\langle \alpha|\hat{A}|\beta\rangle = \langle \beta|\hat{A}|\alpha\rangle^*, \tag{2.17}$$

where $|\alpha\rangle$ and $|\beta\rangle$ are arbitrary states.

The definition of Hermitian operators given above makes it straightforward to prove two theorems proven in Chap. 1 for operators being applied to wavefunctions in one-dimensional space. Namely, the eigenvalues of a Hermitian operator are always real numbers, and two eigenstates of a Hermitian operator with different eigenvalues are always orthogonal. Full statements and proofs of these theorems are provided below.

Theorem 2.1 *Given a Hermitian operator $\hat{A}$, all of its eigenvalues are real numbers.*

Proof Given that $|a\rangle$ is an eigenstate of $\hat{A}$ with finite norm and eigenvalue λ_a, the use of $|\alpha\rangle = |\beta\rangle = |a\rangle$ in Eq. (2.17) leads to the following identity:

$$\lambda_a \langle a|a\rangle = \langle a|\hat{A}|a\rangle = \langle a|\hat{A}|a\rangle^* = \lambda_a^* \langle a|a\rangle. \tag{2.18}$$

Since $\langle a|a\rangle$ is real and is assumed to be nonzero, this identity leads to $\lambda_a = \lambda_a^*$, which is true only when λ_a is a real number. □

Theorem 2.2 *The eigenkets of a Hermitian operator $\hat{A}$ corresponding to different eigenvalues are always orthogonal.*

Proof Let us assume that $|a'\rangle$ and $|a''\rangle$ are eigenkets of $\hat{A}$ with two different eigenvalues, $\lambda_{a'}$ and $\lambda_{a''}$. Then,

$$\langle a'|\hat{A}|a''\rangle = \lambda_{a'}\langle a'|a''\rangle = \lambda_{a''}\langle a'|a''\rangle, \tag{2.19}$$

where the first equality results from applying $\hat{A}$ to $\langle a'|$ and the second equality results from applying $\hat{A}$ to $|a''\rangle$. Since $\lambda_{a'} \neq \lambda_{a''}$, the only possibility that the above equality is true is that $\langle a'|a''\rangle = 0$. This proves the above statement regarding the orthogonality. □

All physical observables correspond to Hermitian operators. If not, one has to accept that complex values can result from the measurement of the physical observable, which is impossible because all the values we deal with are real numbers. Well known examples of physical observables are position and momentum operators, which will be described in more detail in the next subsection. Most importantly, a Hamiltonian operator is Hermitian.

2.3.2 One Dimensional Position Operator and Eigenket

Let us consider a one dimensional position operator $\hat{x}$. Then, one can define a position eigenket $|x\rangle$ such that

$$\hat{x}|x\rangle = x|x\rangle = |x\rangle x. \tag{2.20}$$

Similarly, the action of the position operator on $\langle x|$ is defined by

$$\langle x|\hat{x} = \langle x|x = x\langle x|. \tag{2.21}$$

Then, the Schrödinger's wavefunction, or its value at particular position x, can be defined as an inner product of a state ket with the position bra , $\langle x|$. For example, consider a state $|\alpha\rangle$. Then, the corresponding wavefunction can be defined as

$$\psi_\alpha(x) = \langle x|\alpha\rangle. \tag{2.22}$$

Taking the complex conjugate of this,

$$\psi_\alpha^*(x) = \langle \alpha|x\rangle. \tag{2.23}$$

Combining the above definitions, one can find out the effect of the operation of $\hat{x}$ on an arbitrary state $|\alpha\rangle$ as follows:

$$\langle x|\hat{x}|\alpha\rangle = (\langle x|\hat{x})|\alpha\rangle = x\langle x|\alpha\rangle. \tag{2.24}$$

The set of position eigenkets is always complete as follows:

$$\hat{1} = \int_{-\infty}^{\infty} dx|x\rangle\langle x|. \tag{2.25}$$

This means that the values of wavefunction at all positions provide complete information on the state. This becomes clear by applying the above identity to an arbitrary state as follows:

$$|\alpha\rangle = \hat{1}|\alpha\rangle = \int_{-\infty}^{\infty} dx\ |x\rangle\langle x|\alpha\rangle = \int_{-\infty}^{\infty} dx\ |x\rangle\psi_\alpha(x) = \int_{-\infty}^{\infty} dx\ \psi_\alpha(x)|x\rangle. \tag{2.26}$$

Note that the last equality in the above equation results from $\psi_\alpha(x)$ being a complex number and that its order with respect to the ket does not matter. The above identity implies that the value of a Schrödinger's wavefunction at each x can be viewed as nothing but the coefficient (with the inclusion of integration element dx) in the expansion of the state $|\alpha\rangle$ in terms of the position eigenkets. This also ensures that the normalization condition within the Dirac notation is the same as that involving Schrödinger's wavefunction as follows:

$$\langle\alpha|\alpha\rangle = \langle\alpha|\hat{1}|\alpha\rangle = \int_{-\infty}^{\infty} dx\ \langle\alpha|x\rangle\langle x|\alpha\rangle = \int_{-\infty}^{\infty} dx\ |\psi_\alpha(x)|^2. \tag{2.27}$$

Applying Eq. (2.25) to another position ket, we also find that

$$|x'\rangle = \int_{-\infty}^{\infty} dx\ |x\rangle\langle x|x'\rangle. \tag{2.28}$$

Since the above equation must be true for any value of x', this means that

$$\langle x|x'\rangle = \delta(x - x'), \tag{2.29}$$

where $\delta(x-x')$ is the Dirac-delta function defined in Chap. 1, and is zero for $x \neq x'$ and ∞ for $x = x'$ while its integration is equal to one. Note that this Dirac-delta function is not a genuine function, but can be defined only as a limiting value of a sequence of functions that attain the stated properties. Thus, care should be taken working with the delta function.

2.3.3 One Dimensional Momentum Operator and Eigenket

It was stated in Chap. 1 that measurement of momentum corresponds to taking the first order derivative of the wavefunction, as shown by Eq. (1.24). Let us assume that $\phi_p(x)$ is an eigenfunction of the momentum operator with eigenvalue p. According to Schrödinger's formulation, this should satisfy

$$\frac{\hbar}{i}\frac{\partial}{\partial x}\phi_p(x) = p\phi_p(x). \tag{2.30}$$

A general solution of the above equation is

$$\phi_p(x) = N_p e^{ipx/\hbar}. \tag{2.31}$$

where N_p is a normalization constant. In the Dirac notation, the above eigenfunction of momentum operator can be viewed as the inner product between momentum eigenket and position eigenbra as follows:

$$\phi_p(x) = \langle x|p\rangle, \tag{2.32}$$

where $|p\rangle$ is an eigenstate of the momentum operator satisfying

$$\hat{p}|p\rangle = p|p\rangle. \tag{2.33}$$

As is the case of position ket and bra, the momentum ket and bra are assumed to satisfy the following completeness relation:

$$\hat{1} = \int_{-\infty}^{\infty} dp\ |p\rangle\langle p|. \tag{2.34}$$

Then, the normalization constant N_p can be determined in the following way:

$$\begin{aligned}\delta(x-x') &= \langle x|x'\rangle = \langle x|\hat{1}|x'\rangle = \int_{-\infty}^{\infty} dp\langle x|p\rangle\langle p|x'\rangle \\ &= N_p^2 \int_{-\infty}^{\infty} dp\ e^{ip(x-x')/\hbar} = N_p^2\hbar \int_{-\infty}^{\infty} dk\ e^{ik(x-x')}.\end{aligned} \tag{2.35}$$

This is consistent with the definition of the Dirac-delta function shown in Eq. (1.85) if $N_p^2 = 1/(2\pi\hbar)$. Therefore,

$$\phi_p(x) = \langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}. \tag{2.36}$$

This identity can be used to find out the effect of the operation of $\hat{p}$ on the position eigenket.

2.3.4 Expressions for Momentum Operator

One can show that

$$\langle x|\hat{p}|p\rangle = \langle x|p|p\rangle = p\langle x|p\rangle = \frac{\hbar}{i}\frac{\partial}{\partial x}\langle x|p\rangle. \tag{2.37}$$

Taking complex conjugate of the above equation and noting that $\hat{p}$ is a Hermitian operator, one can find that

$$\langle p|\hat{p}|x\rangle = -\frac{\hbar}{i}\frac{\partial}{\partial x}\langle p|x\rangle = \langle p|\left(-\frac{\hbar}{i}\frac{\partial}{\partial x}|x\rangle\right), \tag{2.38}$$

Since the above relationship holds for any $\langle p|$, this implies that

$$\hat{p}|x\rangle = -\frac{\hbar}{i}\frac{\partial}{\partial x}|x\rangle, \tag{2.39}$$

where

$$-\frac{\hbar}{i}\frac{\partial}{\partial x}|x\rangle = -\frac{\hbar}{i}\lim_{\delta x\to 0}\frac{|x+\delta x\rangle - |x\rangle}{\delta x}. \tag{2.40}$$

Note that the sign on the righthand side of Eq. (2.39) is opposite to that for the Schrödinger's definition of momentum measurement given by Eq. (1.24). In fact, the two is consistent with each other and can be shown to be equivalent if we use a proper version of the Schrödinger's definition for a momentum operation in the Dirac notation as described below.

Taking the Hermitian conjugate of Eq. (2.39) leads to

$$\langle x|\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}\langle x|. \tag{2.41}$$

Now taking the inner product of the above identity with an arbitrary state $|\psi_\alpha\rangle$, one can obtain

$$\langle x|\hat{p}|\psi_\alpha\rangle = \frac{\hbar}{i}\frac{\partial}{\partial x}\langle x|\psi_\alpha\rangle = \frac{\hbar}{i}\frac{\partial}{\partial x}\psi_\alpha(x). \tag{2.42}$$

The above identity is equivalent to Eq. (1.24) if we interpret the left hand side as an application of the momentum operation on a Schrödinger's wavefunction. Note that $\hat{p}\psi_\alpha(x)$ does not make sense in the Dirac notation because an operator can be applied only to either a ket or bra, not to a complex number.

2.3.5 Schrödinger Equations in the Dirac Notation

Time Dependent Schrödinger Equation

The time dependent Schrödinger equation for $|\psi; t\rangle$, a ket representing a quantum mechanical state labeled as ψ and dependent on time t as a parameter, is as follows:

$$i\hbar\frac{\partial}{\partial t}|\psi; t\rangle = \hat{H}|\psi; t\rangle. \tag{2.43}$$

Taking the Hermitian conjugate of the above equation and noting that Hamiltonian operator is Hermitian, the above equation for a ket is equivalent to an equation for the following equation for the corresponding bra.

$$-i\hbar\frac{\partial}{\partial t}\langle\psi; t| = \langle\psi; t|\hat{H}. \tag{2.44}$$

On the other hand, for the case of a stationary state, namely, $|\psi; t\rangle = |\psi\rangle e^{-iEt/\hbar}$, the time independent part of this state satisfies the time independent Schrödinger equation as described below.

Time Independent Schrödinger Equation

The time independent Schrödinger equation for a stationary eigenket $|\psi\rangle$ of a Hamiltonian $\hat{H}$ with eigenvalue E is

$$\hat{H}|\psi\rangle = E|\psi\rangle. \tag{2.45}$$

The above equation for an eigenket is equivalent to the following equation for the corresponding bra.

$$\langle\psi|\hat{H} = E\langle\psi|. \tag{2.46}$$

For a particle with mass m in one dimension subject to a potential energy $V(x)$, the Hamiltonian operator is defined

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x}). \tag{2.47}$$

Note that the above expression is the same as the first form in Eq. (1.28). However, note that the second form in this equation has its meaning only when projected to the position state. In the Dirac notation, this is realized by taking the inner product of the Schrödinger equation with the position state. For example, taking the inner product of Eq. (2.45) with $\langle x|$, we find that

$$\begin{aligned}\langle x|\hat{H}|\psi\rangle &= \langle x|\left(\frac{\hat{p}^2}{2m} + \hat{V}(\hat{x})\right)|\psi\rangle \\ &= \left(\frac{1}{2m}\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 + V(x)\right)\langle x|\psi\rangle \\ &= \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi(x) = E\psi(x),\end{aligned} \tag{2.48}$$

where we have used the identity of Eq. (2.41) twice in obtaining the second equality and used the definition of $\psi(x) = \langle x|\psi\rangle$ in the last line. Note that the last line has the same form as the original Schrödinger equation.

2.3.6 Commutator

Given two operators $\hat{A}$ and $\hat{B}$, there are two ways to order them in creating product operations. The difference between them is called a **commutator**, which plays an important role in quantum mechanics and is defined as follows.

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}. \tag{2.49}$$

When the two operators can be measured simultaneously, the above commutator is zero. A good example for two commuting operators is the position operator and any of its function. Namely, for any operator $\hat{A}(\hat{x})$ defined as a function of position operator only, $[\hat{x}, \hat{A}(\hat{x})] = 0$.

If the commutator between two physical observables $\hat{A}$ and $\hat{B}$ is nonzero, it is impossible to measure them simultaneously with arbitrary precision. Rather, the product of uncertainties of the two observables has lower bound given by half the absolute value of the expectation value of the commutator. Appendix of this chapter provides a detailed derivation of this a general uncertainty relationship.

Expressing an operator as a sum of outer products in the Dirac notation makes it straightforward to calculate the commutator. For example, consider two operators $|\alpha\rangle\langle\beta|$ and $|\gamma\rangle\langle\delta|$. The commutator between the two is given by

$$\begin{aligned}[|\alpha\rangle\langle\beta|, |\gamma\rangle\langle\delta|] &= |\alpha\rangle\langle\beta|\gamma\rangle\langle\delta| - |\gamma\rangle\langle\delta|\alpha\rangle\langle\beta| \\ &= (\langle\beta|\gamma\rangle)|\alpha\rangle\langle\delta| - (\langle\delta|\alpha\rangle)|\gamma\rangle\langle\beta|.\end{aligned} \tag{2.50}$$

It is easy to see that this commutator is zero (i) if $|\alpha\rangle = |\gamma\rangle$ and $\langle\beta| = \langle\delta|$, or (ii) $\langle\beta|\gamma\rangle = \langle\delta|\alpha\rangle = 0$.

The commutator with the most fundamental importance in quantum mechanics is that between position and momentum, which is calculated below.

Commutator Between Position and Momentum Operator

Let us first apply $[\hat{x}, \hat{p}]$ to an arbitrary ket $|\alpha\rangle$. Taking the inner product of the resulting ket with $\langle x|$ leads to

$$\begin{aligned}
\langle x|[\hat{x}, \hat{p}]|\alpha\rangle &= \langle x|(\hat{x}\hat{p} - \hat{p}\hat{x})|\alpha\rangle \\
&= \langle x|\hat{x}\hat{p}|\alpha\rangle - \langle x|\hat{p}\hat{x}|\alpha\rangle \\
&= x\langle x|\hat{p}|\alpha\rangle - \frac{\hbar}{i}\frac{\partial}{\partial x}\langle x|\hat{x}|\alpha\rangle \\
&= x\frac{\hbar}{i}\frac{\partial}{\partial x}\langle x|\alpha\rangle - \frac{\hbar}{i}\frac{\partial}{\partial x}x\langle x|\alpha\rangle \\
&= x\frac{\hbar}{i}\frac{\partial}{\partial x}\langle x|\alpha\rangle - \frac{\hbar}{i}\langle x|\alpha\rangle - x\frac{\hbar}{i}\frac{\partial}{\partial x}\langle x|\alpha\rangle \\
&= i\hbar\langle x|\alpha\rangle = \langle x|(i\hbar)|\alpha\rangle.
\end{aligned} \tag{2.51}$$

Since the above identity holds true for arbitrary $\langle x|$ and $|\alpha\rangle$, it implies the following identity:

$$[\hat{x}, \hat{p}] = i\hbar. \tag{2.52}$$

There are a few important rules that commutators satisfy. From the definition of the commutator, it is straightforward to show the following identities:

$$[a\hat{A}, \hat{B}] = [\hat{A}, a\hat{B}] = a[\hat{A}, \hat{B}], \tag{2.53}$$

$$[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}], \tag{2.54}$$

$$[\hat{A} + \hat{B}, \hat{C}] = [\hat{A}, \hat{C}] + [\hat{B}, \hat{C}], \tag{2.55}$$

$$[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}], \tag{2.56}$$

where $\hat{A}$, $\hat{B}$, and $\hat{C}$ are arbitrary operators, and a is an arbitrary complex number.

There is also an important identity involving products between three operators as shown below.

Theorem 2.3 *For any operator $\hat{A}$, $\hat{B}$, and $\hat{C}$, the following identity is always true.*

$$[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}. \tag{2.57}$$

Proof Employing the definition of a commutator given by Eq. (2.49), the lefthand side of the above equation can be expressed as

$$
\begin{aligned}
[\hat{A}\hat{B}, \hat{C}] &= \hat{A}\hat{B}\hat{C} - \hat{A}\hat{C}\hat{B} + \hat{A}\hat{C}\hat{B} - \hat{C}\hat{A}\hat{B} \\
&= \hat{A}(\hat{B}\hat{C} - \hat{C}\hat{B}) + (\hat{A}\hat{C} - \hat{C}\hat{A})\hat{B} \\
&= \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}.
\end{aligned} \tag{2.58}
$$

□

In a similar manner, one can also prove the following identity:

$$
[\hat{A}, \hat{B}\hat{C}] = \hat{B}[\hat{A}, \hat{C}] + [\hat{A}, \hat{B}]\hat{C}. \tag{2.59}
$$

Finally, it is also easy to prove the following Jacobi identity by directly expanding expressions for commutators:

$$
[\hat{A}, [\hat{B}, \hat{C}]] + [\hat{B}, [\hat{C}, \hat{A}]] + [\hat{C}, [\hat{A}, \hat{B}]] = 0. \tag{2.60}
$$

2.3.7 Compatibility and Completeness

Two operators $\hat{A}$ and $\hat{B}$ are called **compatible** when their commutator $[\hat{A}, \hat{B}] = 0$. If two operators are compatible, one can always find the set of simultaneous eigenkets of $\hat{A}$ and $\hat{B}$. A set of operators is called **maximally compatible** if all the operators in this set are compatible and if there is no additional observable that are compatible with all the operators within the set.

A **basis** is a set of linearly independent kets (or equivalently a set of linearly independent bras). The basis is called **orthonormal** if all the kets in the set have the unit norm and are orthogonal to other kets in the set. A basis set consisting of $|n\rangle$'s is called **complete** if it satisfies the following identity:

$$
\sum_n |n\rangle\langle n| = \hat{1}, \tag{2.61}
$$

where n represents the collection of all parameters need to specify each ket. The sum has to become integration if n is a continuous real parameter as in the cases of position or momentum. The set of **simultaneous eigenkets of maximally compatible observables** is orthonormal and complete. The number of such eigenkets is called the dimension of the ket or bra space.

Let us assume that a set of states $|n\rangle$'s forms a complete orthonormal basis in the sense that Eq. (2.61) holds true and that $\langle n|n'\rangle = \delta_{nn'}$. Then, for a given state $|\alpha\rangle$,

$$|\alpha\rangle = \hat{1}|\alpha\rangle = \sum_n |n\rangle\langle n|\alpha\rangle = \sum_n \alpha_n |n\rangle, \tag{2.62}$$

where $\alpha_n = \langle n|\alpha\rangle$. Both associative and distributive rules for inner and outer products have been used in deriving the above equality. Similarly,

$$\langle\alpha| = \langle\alpha|\hat{1} = \sum_n \langle\alpha|n\rangle\langle n| = \sum_n \alpha_n^* \langle n|. \tag{2.63}$$

Taking the inner product between $\langle\alpha|$ and $|\alpha\rangle$ shown above,

$$\begin{aligned}\langle\alpha|\alpha\rangle &= \sum_n \sum_m \langle\alpha|n\rangle\langle n|m\rangle\langle m|\alpha\rangle \\ &= \sum_n \sum_m \langle\alpha|n\rangle\delta_{nm}\langle m|\alpha\rangle = \sum_n |\alpha_n|^2.\end{aligned} \tag{2.64}$$

If $|\alpha\rangle$ is normalized, the above relation implies that $\sum_n |\alpha_n|^2 = 1$.

Given a complete orthonormal basis, it is easy to find an expression for any operator $\hat{A}$ in terms of linear combinations of those involving outer products between states within the basis. This expression can be found by applying Eq. (2.61) on both sides of $\hat{A}$ as follows:

$$\begin{aligned}\hat{A} = \hat{1}\hat{A}\hat{1} &= \sum_n \sum_m |n\rangle\langle n|\hat{A}|m\rangle\langle m| \\ &= \sum_n \sum_m |n\rangle A_{nm}\langle m| = \sum_n \sum_m A_{nm}|n\rangle\langle m|,\end{aligned} \tag{2.65}$$

where $A_{nm} = \langle n|\hat{A}|m\rangle$. For the special case where $|n\rangle$'s are eigenstates of $\hat{A}$, the above expression reduces to $\hat{A} = \sum_n A_n |n\rangle\langle n|$.

2.3.8 Measurement Operator

Measurement in quantum mechanics is in general a complicated process through which an experimental device interacts with a quantum system and produces real numbers as its record [25]. How to understand and define measurement process has remained an important foundational issue of quantum mechanics. Although debates on quantum measurement still continue, it has been shown that it is possible to formulate measurement in a manner fully consistent with the theory of quantum mechanics [26–28] unlike the old Copenhagen interpretation that required *ad hoc*

interaction with classical systems. In addition, there is good consensus that a large class of measurements, at least theoretically, can be represented by well-defined operators.[4]

The simplest operator representing measurement process is called projective measurement. Consider a quantum state $|\psi\rangle$ and a physical observable $\hat{A}$. Assume that a measurement of $\hat{A}$ has produced a real number. If the same measurement of $\hat{A}$ is made immediately afterwards, the same number has to be produced according to the principle of causality. Therefore, the state right after the measurement of $\hat{A}$ has to be an eigenstate of $\hat{A}$ and the outcome of the measurement has to be an eigenvalue of $\hat{A}$. Let us denote this eigenvalue as λ_a and assume that we can identify a single normalized eigenstate $|\lambda_a\rangle$ corresponding to the state right after the measurement. Then, the following projection operator can be used to represent the measurement operation:

$$\hat{P}_{\lambda_a} = |\lambda_a\rangle\langle\lambda_a|. \tag{2.66}$$

Thus, the process of measuring λ_a for a given state $|\psi\rangle$ amounts to $\hat{P}_{\lambda_a}|\psi\rangle = |\lambda_a\rangle\langle\lambda_a|\psi\rangle$, and the probability of having this outcome is given by $|\langle\lambda_a|\psi\rangle|^2$.

More generally, let us assume that it is possible to identify all observables compatible with $\hat{A}$. Then, denoting the set of all eigenvalues for the operators as ξ, we can identify eigenstates, $|\lambda_a, \xi\rangle$'s, which are orthonormal and complete. Thus,

$$\hat{1} = \sum_{\lambda_a,\xi} |\lambda_a, \xi\rangle\langle\lambda_a, \xi|. \tag{2.67}$$

Then, the least intrusive projective measurement of λ_a is represented by

$$\hat{P}_{\lambda_a} = \sum_{\xi} |\lambda_a, \xi\rangle\langle\lambda_a, \xi|. \tag{2.68}$$

The outcome of this measurement is a linear combination of states with different values of ξ,

$$\hat{P}_{\lambda_a}|\psi\rangle = \sum_{\xi} |\lambda_a, \xi\rangle\langle\lambda_a, \xi|\psi\rangle. \tag{2.69}$$

The general projective measurement described above can be extended further to a so called positive operator valued measure (POVM) measurement, which is

[4] This does not yet mean that the issue of quantum measurement is fully settled because there is still large gap between theoretical definition and experimental practice of quantum measurement. It is often the case that reliable experimental realization of fully quantum mechanical measurement is extremely difficult, whereas reliable theoretical modeling of experimentally viable measurement can be challenging.

defined as a nonnegative Hermitian operator $\hat{\Pi}_a$. The subscript a in this operator collectively represents a set of parameters defining the outcome of the measurement, and integration (or summation) of all the operators over all possible values of a leads to the identity operator as follows:

$$\hat{1} = \int da\, \hat{\Pi}_a. \tag{2.70}$$

It is assumed that different $\hat{\Pi}_a$'s do not necessarily commute with each other. The only requirement is that $\hat{\Pi}_a$ is Hermitian and is positive, which means that $\langle\psi|\hat{\Pi}_a|\psi\rangle \geq 0$ for any $|\psi\rangle$. The POVM measurement is more general than projective measurement and can account for physical situations where the details of post-measurement states are not completely specified [25].

2.3.9 Unitary Operator

Definition of Unitary Operator

A unitary operator, denoted as $\hat{U}$ here, satisfies the following condition:

$$\hat{U}^\dagger\hat{U} = \hat{U}\hat{U}^\dagger = \hat{1}. \tag{2.71}$$

In other words, the Hermitian conjugate of a unitary operator corresponds to its inverse operator. This property allows the operator to preserve the norm of any quantum state and also the orthogonality between two states.

Unitary operators are essential components in the formulation of quantum mechanics. Let us consider an arbitrary ket $|\alpha\rangle$, which is not necessarily normalized. Then, let us introduce another ket created by applying a unitary operator to this as follows:

$$|\alpha'\rangle = \hat{U}|\alpha\rangle. \tag{2.72}$$

Note that the above equation does not correspond to any measurement process because $\hat{U}$ is not Hermitian except for the trivial case of the identity operator. Rather, this can simply be viewed as either transformation needed for better representation of quantum states or transition that happens naturally.

The main reason why unitary operators are important is because they conserve the norm and the orthogonality between states. In other words, while the new

transformed state $|\alpha'\rangle$ is different from $|\alpha\rangle$ in general, the two have the same norm as follows:

$$\langle\alpha'|\alpha'\rangle = \left(\langle\alpha|\hat{U}^\dagger\right)\left(\hat{U}|\alpha\rangle\right) = \langle\alpha|\left(\hat{U}^\dagger\hat{U}\right)|\alpha\rangle = \langle\alpha|\hat{1}|\alpha\rangle = \langle\alpha|\alpha\rangle. \tag{2.73}$$

When two orthogonal states are transformed by the same unitary operator, they remain orthogonal as well. Let us consider another ket $|\beta\rangle$ and its unitary transformation as follows:

$$|\beta'\rangle = \hat{U}|\beta\rangle. \tag{2.74}$$

Then, it is also straightforward to show that the inner product between $|\beta'\rangle$ and $|\alpha'\rangle$ remains the same as that between $|\alpha\rangle$ and $|\beta\rangle$ as follows:

$$\langle\beta'|\alpha'\rangle = \left(\langle\beta|\hat{U}^\dagger\right)\left(\hat{U}|\alpha\rangle\right) = \langle\beta|\left(\hat{U}^\dagger\hat{U}\right)|\alpha\rangle = \langle\beta|\hat{1}|\alpha\rangle = \langle\beta|\alpha\rangle. \tag{2.75}$$

Thus, for the case where $\langle\beta|\alpha\rangle = 0$, the above identity implies that $\langle\beta'|\alpha'\rangle = 0$.

An important application of a unitary operator is a transformation from one basis to another. Consider a set of orthonormal states, $|\varphi_n\rangle$'s with $n = 1, 2, \cdots$, satisfying the following completeness relationship:

$$\hat{1} = \sum_{n=1}^{\infty} |\varphi_n\rangle\langle\varphi_n|. \tag{2.76}$$

Thus, these form a complete orthonormal basis. Then, the following set of states created by a unitary transformation,

$$|\varphi'_n\rangle = \hat{U}|\varphi_n\rangle, \ n = 1, 2, 3, \cdots \tag{2.77}$$

remain orthonormal due to Eqs. (2.73) and (2.75). The fact that these satisfy the completeness relationship can also be shown easily. Let us apply $\hat{U}$ on the lefthand side and $\hat{U}^\dagger$ on the righthand side of Eq. (2.76). Then,

$$\hat{1} = \hat{U}\left(\sum_{n=1}^{\infty}|\varphi_n\rangle\langle\varphi_n|\right)\hat{U}^\dagger = \sum_{n=1}^{\infty}\hat{U}|\varphi_n\rangle\langle\varphi_n|\hat{U}^\dagger = \sum_{n=1}^{\infty}|\varphi'_n\rangle\langle\varphi'_n|, \tag{2.78}$$

where the first equality results from the definition of the unitary operator, Eq. (2.71). The above identity indeed proves that $|\varphi'_n\rangle$'s form a complete orthonormal basis.

Given a Hermitian operator $\hat{A}$, the following operator[5] is always a unitary operator.

$$\begin{aligned}\hat{U}_A &= \exp\left\{-\frac{i}{\hbar}\hat{A}\right\} \\ &= 1 - \frac{i}{\hbar}\hat{A} + \frac{1}{2!}\left(\frac{-i}{\hbar}\right)^2 \hat{A}^2 + \cdots + \frac{1}{n!}\left(\frac{-i}{\hbar}\right)^n \hat{A}^n + \cdots \\ &= \cos\left(\hat{A}/\hbar\right) - i\sin\left(\hat{A}/\hbar\right),\end{aligned} \tag{2.79}$$

where the third equality comes from the fact that $e^{-ix} = \cos(x) - i\sin(x)$. The fact that $\hat{U}_A$ is a unitary operator can be proved as follows. Taking the Hermitian conjugate of $\hat{U}_A$, we find that

$$\hat{U}_A^\dagger = \cos\left(\hat{A}/\hbar\right) + i\sin\left(\hat{A}/\hbar\right), \tag{2.80}$$

where $\cos\left(\hat{A}/\hbar\right)$ and $\sin\left(\hat{A}/\hbar\right)$ are Hermitian operators, since they are real functions of a Hermitian operator. Then,

$$\begin{aligned}\hat{U}_A\hat{U}_A^\dagger &= \left(\cos\left(\hat{A}/\hbar\right) - i\sin\left(\hat{A}/\hbar\right)\right)\left(\cos\left(\hat{A}/\hbar\right) + i\sin\left(\hat{A}/\hbar\right)\right) \\ &= \cos^2\left(\hat{A}/\hbar\right) + \sin^2\left(\hat{A}/\hbar\right) = \hat{1},\end{aligned} \tag{2.81}$$

where the last equality comes from the fact that $\cos^2(x) + \sin^2(x) = 1$ and that this identity remains true whether x is a number or an operator. In a similar manner, it is possible to prove that $\hat{U}_A^\dagger\hat{U}_A = \hat{1}$. Therefore, $\hat{U}_A$ is a unitary operator.

A well-known example of the type of the unitary operator given above is the time evolution operator defined below.

Definition of a Time Evolution Operator

For any Hamiltonian operator $\hat{H}$, which is time independent, the corresponding time evolution operator is defined as

$$\hat{U}_H(t) = \exp\left\{-\frac{it}{\hbar}\hat{H}\right\}. \tag{2.82}$$

(continued)

[5] This is an example of the definition for a function $f(\hat{A})$ of an operator $\hat{A}$, which implies substituting $\hat{A}$ for x in the Taylor expansion of $f(x)$.

If we known the complete set of the eigenstates and eigenvalues of the Hamiltonian operator, namely, $|\phi_n\rangle$'s and E_n's with $n = 1, 2, 3, \cdots$ such that $\hat{H}|\phi_n\rangle = E_n|\phi_n\rangle$, the above time evolution operator can also be expressed as

$$\hat{U}_H(t) = \sum_n e^{-iE_n t/\hbar}|\phi_n\rangle\langle\phi_n|. \tag{2.83}$$

It is easy to show that the time evolution operator satisfies the time dependent Schrödinger equation as follows:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\hat{U}_H(t) &= \sum_n i\hbar\left(-\frac{iE_n}{\hbar}\right)e^{-iE_n t/\hbar}|\phi_n\rangle\langle\phi_n| \\ &= \sum_n e^{-iE_n t/\hbar}\hat{H}|\phi_n\rangle\langle\phi_n| \\ &= \hat{H}\hat{U}_H(t). \end{aligned} \tag{2.84}$$

Given an arbitrary state $|\psi\rangle$ at time $t = 0$, the state at arbitrary time t can be expressed as

$$|\psi; t\rangle = \hat{U}_H(t)|\psi\rangle. \tag{2.85}$$

The above state satisfies the time dependent Schrödinger equation as a result of Eq. (2.84).

2.4 Particle in a One-Dimensional Box: Revisited with the Dirac Notation

In Chap. 1, we have determined the eigenvalue, Eq. (1.58), and eigenfunction, Eq. (1.61), for a particle in a one dimensional box. Let us denote the eigenket of the Hamiltonian with eigenvalue E_n as $|n\rangle$. Thus, these satisfy the following time independent Schrödinger equation:

$$\hat{H}|n\rangle = E_n|n\rangle,\ n = 1, 2, \cdots, \tag{2.86}$$

where the full information on $|n\rangle$ can be obtained from

$$\langle x|n\rangle = \begin{cases} \sqrt{2/l}\sin(n\pi x/l) & , \ 0 < x < l \\ 0 & , \ x \le 0 \text{ or } x \ge l \end{cases} \tag{2.87}$$

Since the above function is real, $\langle n|x\rangle = \langle x|n\rangle$. The set of eigenstates given above is orthonormal as follows:

$$\begin{aligned}\langle n|m\rangle &= \int_{-\infty}^{\infty} dx \langle n|x\rangle\langle x|m\rangle \\ &= \frac{2}{l}\int_0^l dx\ \sin\left(\frac{n\pi x}{l}\right)\sin\left(\frac{m\pi x}{l}\right) \\ &= \frac{1}{l}\int_0^l dx\ \left[\cos\left(\frac{(n-m)\pi x}{l}\right) - \cos\left(\frac{(n+m)\pi x}{l}\right)\right] \\ &= \delta_{nm}.\end{aligned} \tag{2.88}$$

These eigenstates form a complete orthonormal basis and can be used to represent any quantum state as a linear combination. Let us consider a quantum state $|\psi\rangle$ given by a linear combination of eigenstates as follows:

$$|\psi\rangle = \sum_{n=1}^{\infty} C_n|n\rangle. \tag{2.89}$$

This state $|\psi\rangle$ is assumed to be normalized and therefore satisfies the following normalization condition:

$$\langle\psi|\psi\rangle = \sum_{n=1}^{\infty}\sum_{n'=1}^{\infty} C_n^* C_{n'}\langle n|n'\rangle = \sum_{n=1}^{\infty}|C_n|^2 = 1. \tag{2.90}$$

Given that the state $|\psi\rangle$ is the state at time $t = 0$, the state at another time t is fully determined as follows:

$$|\psi; t\rangle = \hat{U}_H(t)|\psi\rangle = \sum_{n=1}^{\infty} C_n\hat{U}_H(t)|n\rangle = \sum_{n=1}^{\infty} C_n e^{-iE_n t/\hbar}|n\rangle, \tag{2.91}$$

where E_n has been defined by Eq. (1.58).

2.5 Direct Product

The direct product is different from the inner or outer product in that it is not an operation involving ket (bra) and bra (ket), but rather represents an expansion of the vector space or its dimensionality.[6] A direct product can be defined between any two

[6] Note that the dimensionality of the vector space is different from that of the space, and can often be infinite.

independent ket (bra) spaces, each with any dimension, resulting in a combined ket (bra) space with higher dimension. For example, if a ket $|\alpha\rangle$ is defined in a ket space $\mathcal{A}$ with dimension N and another ket $|\beta\rangle$ is defined in a ket space $\mathcal{B}$ with dimension M, one can define the following ket

$$|\alpha, \beta\rangle \equiv |\alpha\rangle \otimes |\beta\rangle = |\alpha\rangle|\beta\rangle, \tag{2.92}$$

which is defined in the direct product space $\mathcal{A} \otimes \mathcal{B}$ of dimension $M \times N$. The second equality in the above expression is often used as an abbreviation for the first form and should not be confused with incorrect notation for inner or outer product.

A good example of the direct product is the three dimensional position state. For a three-dimensional position vector expressed in Cartesian coordinate system as $\mathbf{r} = x\mathbf{e}_x + y\mathbf{e}_y + z\mathbf{e}_z$, one can define the corresponding position state employing direct product as follows:

$$|\mathbf{r}\rangle \equiv |x\rangle \otimes |y\rangle \otimes |z\rangle = |x\rangle|y\rangle|z\rangle. \tag{2.93}$$

This is an eigenstate of the position operator $\hat{\mathbf{r}} = \hat{x}\mathbf{e}_x + \hat{y}\mathbf{e}_y + \hat{z}\mathbf{e}_z$ as follows:

$$\hat{\mathbf{r}}|\mathbf{r}\rangle = \mathbf{r}|\mathbf{r}\rangle. \tag{2.94}$$

Similarly, for a three dimensional momentum vector defined in Cartesian coordinate system as $\mathbf{p} = p_x\mathbf{e}_x + p_y\mathbf{e}_y + p_z\mathbf{e}_z$, one can define the three dimensional momentum state employing the direct product as follows:

$$|\mathbf{p}\rangle \equiv |p_x\rangle \otimes |p_y\rangle \otimes |p_z\rangle = |p_x\rangle|p_y\rangle|p_z\rangle. \tag{2.95}$$

This is an eigenstate of the momentum operator $\hat{\mathbf{p}} = \hat{p}_x\mathbf{e}_x + \hat{p}_y\mathbf{e}_y + \hat{p}_z\mathbf{e}_z$ as follows:

$$\hat{\mathbf{p}}|\mathbf{p}\rangle = \mathbf{p}|\mathbf{p}\rangle. \tag{2.96}$$

The direct product can be used to define a state for many particle systems. For example, one can define the position and momentum kets of two particles:

$$|\mathbf{r}_1, \mathbf{r}_2\rangle \equiv |\mathbf{r}_1\rangle \otimes |\mathbf{r}_2\rangle = |\mathbf{r}_1\rangle|\mathbf{r}_2\rangle, \tag{2.97}$$

$$|\mathbf{p}_1, \mathbf{p}_2\rangle \equiv |\mathbf{p}_1\rangle \otimes |\mathbf{p}_2\rangle = |\mathbf{p}_1\rangle|\mathbf{p}_2\rangle. \tag{2.98}$$

For a system with N particles, one can construct position and momentum vector states by expanding the above direct products. It is assumed that the sets of $3N$ dimensional position or momentum vector states constructed this way can be used to completely specify the quantum state of the N particle system.

2.6 Summary and Questions

The Dirac notation provides an efficient and general way to represent states and rules of quantum mechanics. In this notation, Schrödinger's formulation of quantum mechanics employing wavefunction and differential operators can be viewed as a position representation of quantum mechanics.

In the Dirac notation, a quantum state is represented by either ket $|\cdots\rangle$ or bra $\langle\cdots|$, where $\cdots$ can be any index or symbol employed to label the state. Any complex-valued linear combination of kets (bras) belonging to the same ket (bra) space becomes a ket (bra) in the same ket (bra) space, which in general represents a different quantum state. An inner product can always be defined between a bra and a ket defined in these equivalent bra and ket spaces, as in Eq. (2.3), and is a complex number in general.

If the ket and bra represent the same state, the inner product becomes a nonnegative real number and is considered as the magnitude of the state. Quantum mechanically, this magnitude does not have any physical significance. Thus, any ket or bra normalized to have unit magnitude is a convenient choice to carry all the necessary quantum mechanical information.

The inner product between normalized ket and bra can be viewed as indicating the dependence on each other, and its absolute value is always smaller than one if they represent two different states. If the inner product becomes zero, the two state is called orthogonal. Orthonormal states are orthogonal and normalized states, and serve as convenient choice to span either the ket or bra space. If a set of orthonormal states can be used to represent any state as a linear combination, it is called a complete orthonormal basis.

Outer products can also be defined between any ket in a ket space and another bra in the equivalent bra space, as in Eq. (2.6), and can be used to represent an operator or a mapping that transforms a ket (bra) to another ket (bra) in the same ket (bra) space.

Given an operator, its Hermitian conjugate is defined by Eq. (2.11). An operator is called Hermitian if it is the same as its Hermitian conjugate. Eigenvalues of a Hermitian operator are always real and can be used to represent all physical observables including the Hamiltonian. Two operators are called compatible if the commutator between the two, as defined in Eq. (2.49), is zero. The position and momentum operators are not compatible since their commutator is nonzero as shown by Eq. (2.52). Eigenstates of maximally compatible physical observables can be used to form a complete orthonormal basis. The measurement operator can be defined as an outer product of a state with itself, sum of such outer products, or sum of positive Hermitian operators.

The Hermitian conjugate of a unitary operator is its inverse and satisfies the relationship of Eq. (2.71). The inner product between a ket and a bra remains the same even after they are transformed by a unitary operator. All time evolution operators, which satisfy the time dependent Schrödinger equation, are unitary.

Direct product can be formed between any kets (bras) from different and independent ket (bra) spaces, and are used to expand the ket (bra) space. The new space formed this way is called direct product space. Operators in this direct product space are defined as outer products of corresponding kets and bras in the direct product space.

Questions

- How is a ket or bra space defined?
- Is the inner product between a ket and its corresponding bra always nonnegative?
- Can any linear combination of outer products of kets and bras in the Dirac notation represent a physical observable?
- How is an eigenket or eigenbra defined for a given operator?
- Why is Hermitian operator important in quantum mechanics?
- When do two operators become compatible with each other?
- How can the identity operator be expressed in terms of complete orthonormal basis states?
- What is the major difference between projective measurement and POVM measurement?
- How is time evolution operator defined for a given time independent Hamiltonian operator?
- When can a direct product space be formed?
- How can an operator defined in a given ket and bra space be extended to a new direct product space?

Appendix: Cauchy-Schwarz Inequality and a General Uncertainty Relationship

The fact that a ket or bra space forms a well defined normed vector space means that the inner product between any two states satisfies the Cauchy-Schwartz inequality. The statement of this inequality and its proof [6] are summarized below.

Theorem 2.4 *Cauchy-Schwartz inequality: For any states* $|\alpha\rangle$ *and* $|\beta\rangle$*, which have nonzero norms, the following inequality always holds:*

$$|\langle\alpha|\beta\rangle|^2 \leq \langle\alpha|\alpha\rangle\langle\beta|\beta\rangle \tag{2.99}$$

Proof Consider the following linear combination of $|\alpha\rangle$ and $|\beta\rangle$:

$$|\gamma\rangle = |\alpha\rangle + C|\beta\rangle. \tag{2.100}$$

Then, since the inner product of any ket with its corresponding bra is always nonnegative,

$$\begin{aligned}\langle\gamma|\gamma\rangle &= (\langle\alpha| + C^*\langle\beta|)(|\alpha\rangle + C|\beta\rangle) \\ &= \langle\alpha|\alpha\rangle + C^*\langle\beta|\alpha\rangle + C\langle\alpha|\beta\rangle + |C|^2\langle\beta|\beta\rangle \geq 0. \end{aligned} \tag{2.101}$$

Let us choose

$$C = -\frac{\langle\beta|\alpha\rangle}{\langle\beta|\beta\rangle}. \tag{2.102}$$

Employing the above expression in Eq. (2.101), we find that

$$\langle\alpha|\alpha\rangle - \frac{\langle\alpha|\beta\rangle}{\langle\beta|\beta\rangle}\langle\beta|\alpha\rangle - \frac{\langle\beta|\alpha\rangle}{\langle\beta|\beta\rangle}\langle\alpha|\beta\rangle + \frac{|\langle\alpha|\beta\rangle|^2}{\langle\beta|\beta\rangle^2}\langle\beta|\beta\rangle = \frac{\langle\alpha|\alpha\rangle\langle\beta|\beta\rangle - |\langle\alpha|\beta\rangle|^2}{\langle\beta|\beta\rangle} \geq 0. \tag{2.103}$$

Since $\langle\beta|\beta\rangle > 0$, the above inequality implies that

$$\langle\alpha|\alpha\rangle\langle\beta|\beta\rangle - |\langle\alpha|\beta\rangle|^2 \geq 0, \tag{2.104}$$

which completes the proof. □

For the case where $|\alpha\rangle$ and $|\beta\rangle$ are normalized, the above theorem shows that the magnitude of the inner product between the two cannot be greater than 1.

The above Cauchy-Schwarz inequality can be used to prove general uncertainty relationship between two non-commuting operators $\hat{A}$ and $\hat{B}$ as stated below [6].

Theorem 2.5 *For two Hermitian operators $\hat{A}$ and $\hat{B}$ and for any state $|\psi\rangle$, the following inequality holds.*

$$\langle\psi|\Delta\hat{A}^2|\psi\rangle\langle\psi|\Delta\hat{B}^2|\psi\rangle \geq \frac{1}{4}\left|\langle\psi|[\hat{A},\hat{B}]|\psi\rangle\right|^2, \tag{2.105}$$

where $\Delta\hat{A} = \hat{A} - \langle\psi|\hat{A}|\psi\rangle$ and $\Delta\hat{B} = \hat{B} - \langle\psi|\hat{B}|\psi\rangle$.

Proof Let us introduce $|\alpha\rangle = \Delta\hat{A}|\psi\rangle$ and $|\beta\rangle = \Delta\hat{B}|\psi\rangle$. Then, according to the Cauchy-Schwarz inequality proven above,

$$\langle\psi|\Delta\hat{A}^2|\psi\rangle\langle\psi|\Delta\hat{B}^2|\psi\rangle = \langle\alpha|\alpha\rangle\langle\beta|\beta\rangle \geq |\langle\alpha|\beta\rangle|^2. \tag{2.106}$$

Employing the definitions of $|\alpha\rangle$ and $|\beta\rangle$, we find that

$$\begin{aligned}\langle\alpha|\beta\rangle = \langle\psi|\Delta\hat{A}\Delta\hat{B}|\psi\rangle &= \frac{1}{2}\langle\psi|[\Delta\hat{A},\Delta\hat{B}]|\psi\rangle + \frac{1}{2}\langle\psi|(\Delta\hat{A}\Delta\hat{B} + \Delta\hat{B}\Delta\hat{A})|\psi\rangle \\ &= \frac{1}{2}\langle\psi|[\hat{A},\hat{B}]|\psi\rangle + \frac{1}{2}\langle\psi|(\Delta\hat{A}\Delta\hat{B} + \Delta\hat{B}\Delta\hat{A})|\psi\rangle, \end{aligned} \tag{2.107}$$

where in the second equality, the fact that $[\Delta\hat{A}, \Delta\hat{B}] = [\hat{A}, \hat{B}]$ has been used. Note that

$$\Big(\langle\psi|[\hat{A}, \hat{B}]|\psi\rangle\Big)^* = \langle\psi|[\hat{B}, \hat{A}]|\psi\rangle = -\langle\psi|[\hat{A}, \hat{B}]|\psi\rangle, \tag{2.108}$$

which indicates that this is an imaginary number. On the other hand,

$$\Big(\langle\psi|(\Delta\hat{A}\Delta\hat{B} + \Delta\hat{B}\Delta\hat{A})|\psi\rangle\Big)^* = \langle\psi|(\Delta\hat{A}\Delta\hat{B} + \Delta\hat{B}\Delta\hat{A})|\psi\rangle, \tag{2.109}$$

which indicates that this is a real number. Since the square of the absolute value of a complex number is equal to the sum of those for real and imaginary parts,

$$\begin{aligned}\Big|\langle\psi|\Delta\hat{A}\Delta\hat{B}|\psi\rangle\Big|^2 &= \frac{1}{4}\Big|\langle\psi|[\hat{A}, \hat{B}]|\psi\rangle\Big|^2 + \frac{1}{4}\Big|\langle\psi|(\Delta\hat{A}\Delta\hat{B} + \Delta\hat{B}\Delta\hat{A})|\psi\rangle\Big|^2 \\ &\geq \frac{1}{4}\Big|\langle\psi|[\hat{A}, \hat{B}]|\psi\rangle\Big|^2 .\end{aligned} \tag{2.110}$$

Combining the above inequality with Eqs. (2.106) and (2.107), we find that the general uncertainty relationship of Eq. (2.105) is always satisfied. This completes the proof. □

For the two physical observables $\hat{A}$ and $\hat{B}$ and the given state $|\psi\rangle$, let us define uncertainties of the two physical observables as $\Delta A = \sqrt{\langle\psi|\Delta\hat{A}^2|\psi\rangle}$ and $\Delta B = \sqrt{\langle\psi|\Delta\hat{B}^2|\psi\rangle}$. Then, Eq. (2.105) implies that

$$\Delta A \Delta B \geq \frac{1}{2}\Big|\langle\psi|[\hat{A}, \hat{B}]|\psi\rangle\Big|, \tag{2.111}$$

which is the general uncertainty relationship that holds between any two non-commuting physical observables. For the case where $\hat{A} = \hat{x}$ and $\hat{B} = \hat{p}$, namely position and momentum operators, $[\hat{x}, \hat{p}] = i\hbar$. Therefore, $\Delta x \Delta p \geq \hbar/2$, which is a precise statement of Heisenberg's uncertainty principle.

Exercise Problems with Solutions

2.1 Two states $|\alpha\rangle$ and $|\beta\rangle$ are normalized and orthogonal to each other. Given the two states $|a\rangle$ and $|b\rangle$ defined as follows:

$$|a\rangle = |\alpha\rangle + 3i|\beta\rangle,$$
$$|b\rangle = 2i|\alpha\rangle - |\beta\rangle,$$

calculate $\langle a|a\rangle$, $\langle b|b\rangle$, $\langle a|b\rangle$, and $\langle b|a\rangle$, which are all real or complex numbers.

Solution 2.1 The four inner products can be calculated using the fact that $\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1$ and $\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$ as follows:

$$\begin{aligned}
\langle a|a\rangle &= (\langle\alpha - 3i\langle\beta|)(|\alpha\rangle + 3i|\beta\rangle) \\
&= 1 + 9 = 10, \\
\langle b|b\rangle &= (-2i\langle\alpha| - \langle\beta|)(2i|\alpha\rangle - |\beta\rangle) \\
&= 4 + 1 = 5, \\
\langle a|b\rangle &= (\langle\alpha - 3i\langle\beta|)(2i|\alpha\rangle - |\beta\rangle) \\
&= 2i + 3i = 5i, \\
\langle b|a\rangle &= (-2i\langle\alpha| - \langle\beta|)(|\alpha\rangle + 3i|\beta\rangle) \\
&= -2i - 3i = -5i.
\end{aligned}$$

2.2 Two states $|\alpha\rangle$ and $|\beta\rangle$ are normalized and orthogonal to each other. A state $|1\rangle$ is given by the following linear combination.

$$|1\rangle = \frac{1}{\sqrt{2}}(|\alpha\rangle + |\beta\rangle).$$

Show that the above state is normalized. Find another state $|2\rangle$ given by a different linear combination of $|\alpha\rangle$ and $|\beta\rangle$, which is orthogonal to $|1\rangle$ and is normalized.

Solution 2.2 First, let us prove that $|1\rangle$ is normalized. Taking inner product of this with itself, we find that

$$\begin{aligned}
\langle 1|1\rangle &= \frac{1}{2}(\langle\alpha| + \langle\beta|)(|\alpha\rangle + |\beta\rangle) \\
&= = \frac{1}{2}(1 + 1) = 1.
\end{aligned}$$

Second, let us assume a state $|2\rangle = C_\alpha|\alpha\rangle + C_\beta|\beta\rangle$. For this state to be orthogonal to $|1\rangle$,

$$\begin{aligned}
\langle 1|2\rangle &= \frac{1}{\sqrt{2}}(\langle\alpha| + \langle\beta|)\left(C_\alpha|\alpha\rangle + C_\beta|\beta\rangle\right) \\
&= \frac{C_\alpha}{\sqrt{2}}\langle\alpha|\alpha\rangle + \frac{C_\beta}{\sqrt{2}}\langle\beta|\beta\rangle = \frac{1}{\sqrt{2}}\left(C_\alpha + C_\beta\right) = 0.
\end{aligned}$$

For the above condition to be satisfied, $C_\beta = -C_\alpha$. Since $|2\rangle$ has to be normalized,

$$1 = \langle 2|2\rangle = |C_\alpha|^2 + |C_\beta|^2 = 2|C_\alpha|^2.$$

The above condition can be satisfied by choosing $C_\alpha = 1/\sqrt{2}$. Note that this can be multiplied by any unit normal complex value but let us make the simplest choice that C_α is real and positive as assumed. Then, $C_\beta = -1/\sqrt{2}$. As a result, the state $|2\rangle$ is given by

$$|2\rangle = \frac{1}{\sqrt{2}} \left(|\alpha\rangle - |\beta\rangle \right).$$

2.3 Two states $|\alpha\rangle$ and $|\beta\rangle$ are normalized and orthogonal to each other, in terms of which two operators $\hat{A}$ and $\hat{B}$ are defined as follows:

$$\hat{A} = |\alpha\rangle\langle\alpha| - |\beta\rangle\langle\beta|$$
$$\hat{B} = -i|\alpha\rangle\langle\beta| + i|\beta\rangle\langle\alpha|$$

Then, express the following two operators, $\hat{A}\hat{B} + \hat{B}\hat{A}$ and $i\hat{A}\hat{B} - i\hat{B}\hat{A}$ in terms of linear combinations of outer products, $|\alpha\rangle\langle\alpha|$, $|\beta\rangle\langle\beta|$, $|\alpha\rangle\langle\beta|$, and $|\beta\rangle\langle\alpha|$. Make sure that you have the simplest possible forms. State whether each of the two operators is Hermitian or not, and justify your answers.

Solution 2.3 The products $\hat{A}\hat{B}$ and $\hat{B}\hat{A}$ can be calculated as follows:

$$\begin{aligned}
\hat{A}\hat{B} &= \left(|\alpha\rangle\langle\alpha| - |\beta\rangle\langle\beta| \right) \left(-i|\alpha\rangle\langle\beta| + i|\beta\rangle\langle\alpha| \right) \\
&= -i|\alpha\rangle\langle\beta| - i|\beta\rangle\langle\alpha|, \\
\hat{B}\hat{A} &= \left(-|\alpha\rangle\langle\beta| + |\beta\rangle\langle\alpha| \right) \left(|\alpha\rangle\langle\alpha| - i|\beta\rangle\langle\beta| \right) \\
&= i|\alpha\rangle\langle\beta| + i|\beta\rangle\langle\alpha|,
\end{aligned}$$

Summing the above two operators,

$$\begin{aligned}
&\hat{A}\hat{B} + \hat{B}\hat{A} = 0, \\
&i\hat{A}\hat{B} - i\hat{B}\hat{A} = 2 \left(|\alpha\rangle\langle\beta| + |\beta\rangle\langle\alpha| \right).
\end{aligned}$$

Therefore, both $\hat{A}\hat{B} + \hat{B}\hat{A}$ and $i\hat{A}\hat{B} - i\hat{B}\hat{A}$ are Hermitian.

2.4 The following operators are not Hermitian. Add additional (minimum number of) terms and make these operators Hermitian.

(a) $2|\alpha\rangle\langle\alpha| + (3 + 2i)|\alpha\rangle\langle\beta|$

(b) $|1\rangle\langle 1|2\rangle\langle 2| + |2\rangle\langle 3|3\rangle\langle 3|$

(c) $|1\rangle\langle 2| + i|2\rangle\langle 3| + |3\rangle\langle 3|$

(d) $|\alpha\rangle\langle\alpha| - |\beta\rangle\langle\alpha|$

Solution 2.4 Corrected Hermitian operators with minimal number of terms added are provided below.

(a) $2|\alpha\rangle\langle\alpha| + (3+2i)|\alpha\rangle\langle\beta| + (3-2i)|\beta\rangle\langle\alpha|$

(b) $|1\rangle\langle 1|2\rangle\langle 2| + |2\rangle\langle 2|1\rangle\langle 1| + |2\rangle\langle 3|3\rangle\langle 3| + |3\rangle\langle 3|3\rangle\langle 2|$

(c) $|1\rangle\langle 2| + |2\rangle\langle 1| + i|2\rangle\langle 3| - i|3\rangle\langle 2| + |3\rangle\langle 3|$

(d) $|\alpha\rangle\langle\alpha| - |\beta\rangle\langle\alpha| - |\alpha\rangle\langle\beta|$

2.5 For the following functions of operators, which are not necessarily Hermitian, determine the Hermitian conjugate for each function of operators. The answer should be expressed in terms of given operators and their Hermitian conjugates.

(a) $\hat{O}^2 + \hat{O}$

(b) $\hat{O}^2 + i\hat{O}$

(c) $\hat{O}_1\hat{O}_2 + i(\hat{O}_1 + \hat{O}_2)$

(d) $\hat{O}_1\hat{O}_2\hat{O}_3$

Solution 2.5 Hermitian conjugates are provided below.

(a) $\left(\hat{O}^\dagger\right)^2 + \hat{O}^\dagger$

(b) $\left(\hat{O}^\dagger\right)^2 - i\hat{O}^\dagger$

(c) $\hat{O}_2^\dagger\hat{O}_1^\dagger - i\left(\hat{O}_1^\dagger + \hat{O}_2^\dagger\right)$

(d) $\hat{O}_3^\dagger\hat{O}_2^\dagger\hat{O}_1^\dagger$

2.6 Prove the following identities.

$(a)\ [\hat{x}, \hat{p}^2] = 2i\hbar\hat{p}$

$(b)\ [\hat{p}, \hat{x}^2] = -2i\hbar\hat{x}$

Solution 2.6 The above identities can be proved by employing Eq. (2.57) as follows.

(a) $[\hat{x}, \hat{p}^2] = \hat{p}[\hat{x}, \hat{p}] + [\hat{x}, \hat{p}]\hat{p} = i\hbar\hat{p} + i\hbar\hat{p} = 2i\hbar\hat{p}$

(b) $[\hat{p}, \hat{x}^2] = \hat{x}[\hat{p}, \hat{x}] + [\hat{p}, \hat{x}]\hat{x} = -i\hbar\hat{x} - i\hbar\hat{x} = -2i\hbar\hat{x}$

2.7 It is known that $\hat{U}(\theta)$ defined below is unitary for any value of its parameter θ.

$$\hat{U}(\theta) = \cos\theta - i\sin\theta\hat{A},$$

where $\hat{A}$ is a Hermitian operator. Find out the property that $\hat{A}$ should satisfy for the above statement to be true.

Solution 2.7 For the given operator to be unitary,

$$\begin{aligned}\hat{U}(\theta)\hat{U}^{\dagger}(\theta) &= (\cos\theta - i\sin\theta\hat{A})(\cos\theta + i\sin\theta\hat{A}) \\ &= \cos^2\theta - i\sin\theta\cos\theta\hat{A} + i\sin\theta\cos\theta\hat{A} + \sin^2\theta\hat{A}^2 \\ &= \cos^2\theta + \sin^2\theta + \sin^2\theta(\hat{A}^2 - 1) = 1 + \sin^2\theta(\hat{A}^2 - 1) = 1.\end{aligned}$$

For the above identity to be true, $\hat{A}^2 = 1$. For this case, it is also easy to show that $\hat{U}^{\dagger}(\theta)\hat{U}(\theta) = 1$ as well.

2.8 A quantum particle of unit mass in one dimensional box of unit length is prepared in the following state at time $t = 0$.

$$|\psi\rangle = \frac{1}{\sqrt{2}}|E_1\rangle - \frac{i}{\sqrt{2}}|E_3\rangle,$$

where $|E_1\rangle$ and $|E_3\rangle$ are the first and third eigenstates of the Hamiltonian of the particle. Answer the following questions.

(a) Find out the expression for $\langle x|\psi\rangle$.
(b) Determine the state $|\psi; t\rangle$ at time $t = 1$.
(c) Calculate the expression for the expectation value for $\hat{x}$ of the particle for arbitrary time t.

Solution 2.8 For particle in a box of unit length, the eigenvalue and eigenfunction of the Hamiltonian are given by

$$\begin{aligned}E_n &= \frac{\hbar^2}{2}\pi^2 n^2, \\ \langle x|E_n\rangle &= \sqrt{2}\sin(n\pi x),\end{aligned}$$

where $n = 1, 2, \ldots$. Answers for (a), (b), and (c) are provided below.

(a)

$$\begin{aligned}\langle x|\psi\rangle &= \frac{1}{\sqrt{2}}\langle x|E_1\rangle - \frac{i}{\sqrt{2}}\langle x|E_3\rangle \\ &= \frac{\sqrt{2}}{\sqrt{2}}\sin(\pi x) - i\frac{\sqrt{2}}{\sqrt{2}}\sin(3\pi x) \\ &= \sin(\pi x) - i\sin(3\pi x)\end{aligned}$$

(b)

$$|\psi; t\rangle = \frac{1}{\sqrt{2}}e^{-iE_1 t/\hbar}|E_1\rangle - \frac{i}{\sqrt{2}}e^{-iE_3 t/\hbar}|E_3\rangle$$

$$= \frac{1}{\sqrt{2}} e^{-i\hbar\pi^2 t/2} |E_1\rangle - \frac{i}{\sqrt{2}} e^{-i9\hbar\pi^2 t/2} |E_3\rangle$$

For $t = 1$, the above state becomes

$$|\psi; t = 1\rangle = \frac{1}{\sqrt{2}} e^{-i\hbar\pi^2/2} |E_1\rangle - \frac{i}{\sqrt{2}} e^{-i9\hbar\pi^2/2} |E_3\rangle$$

(c)

$$\begin{aligned}
\langle\psi; t|\hat{x}|\psi; t\rangle &= \int_{-\infty}^{\infty} dx \langle\psi; t|x\rangle x \langle x|\psi; t\rangle \\
&= \int_0^1 dx \left(\frac{1}{\sqrt{2}} e^{i\hbar\pi^2 t/2} \langle E_1|x\rangle + \frac{i}{\sqrt{2}} e^{i9\hbar\pi^2 t/2} \langle E_3|x\rangle \right) x \\
&\quad \times \left(\frac{1}{\sqrt{2}} e^{-i\hbar\pi^2 t/2} \langle x|E_1\rangle - \frac{i}{\sqrt{2}} e^{-i9\hbar\pi^2 t/2} \langle x|E_3\rangle \right) \\
&= \int_0^1 dx \left\{ \sin^2(\pi x) x - 2\sin(4\hbar^2\pi^2 t)\sin(\pi x)\sin(3\pi x) x \right. \\
&\quad \left. + \sin^2(3\pi x) x \right\} \\
&= \int_0^1 dx \left\{ \frac{x}{2}(1 - \cos(2\pi x)) - x\sin(4\hbar^2\pi^2 t)(\cos(2\pi x) \right. \\
&\quad \left. - \cos(4\pi x)) + \frac{x}{2}(1 - \cos(6\pi x)) \right\} = \frac{1}{2}.
\end{aligned}$$

Problems

2.9 Given two states $|\alpha\rangle$ and $|\beta\rangle$, which are normalized and orthogonal to each other, answer the following questions.

(a) Given two states $|1\rangle = C(|\alpha\rangle + i|\beta\rangle)$ and $|2\rangle = C(|\alpha\rangle - i|\beta\rangle)$, prove that these two states are orthogonal to each other and determine a real positive number C such that they are normalized.

(b) An operator $\hat{A}$ is defined as $\hat{A} = |1\rangle\langle 2| + |2\rangle\langle 1|$. Find out the expression for $\hat{A}$ in terms of outer products involving $|\alpha\rangle$ and $|\beta\rangle$.

(c) Determine the eigenstates and eigenvalues of $\hat{A}$ given above.

2.10 Prove the following identity:

$$\left[[\hat{x}\hat{p} + \hat{p}\hat{x}, \hat{x}], \hat{p} \right] = 2\hbar^2.$$

2.11 For arbitrary state $|\alpha\rangle$,

$$\langle x|(\hat{x}+\hat{p})^2|\alpha\rangle = \hat{O}(x)\psi_\alpha(x),$$

where $\psi_\alpha(x) = \langle x|\alpha\rangle$ and $\hat{O}(x)$ is a mathematical operator (or an operator in Schrödinger's formulation) that involves functions of x and its derivative. Find out the expression for $\hat{O}(x)$.

2.12 Prove the identity given by Eq. (2.59).

2.13 Prove the Jacobi identity given by Eq. (2.60).

2.14 Use some of the identities provided in the main text and simplify $[\hat{p}^2+\hat{x}^2, \hat{p}\hat{x}]$ as much as possible, where $\hat{x}$ is the position operator and $\hat{p}$ is the momentum operator along the same direction.

2.15 A quantum particle of unit mass in one dimensional box of unit length is prepared in the following state at time $t = 0$.

$$|\psi\rangle = \frac{\sqrt{3}}{2}|E_1\rangle| + \frac{i}{2}|E_2\rangle,$$

where $|E_1\rangle$ and $|E_2\rangle$ are the first and second eigenstates of the Hamiltonian of the particle. Answer the following questions.

(a) Find out the expression for $\langle x|\psi\rangle$.
(b) Determine the state $|\psi; t\rangle$ at time $t = 1$.
(c) Calculate the expression for the expectation value for $\hat{x}$ of the particle for arbitrary time t.

Chapter 3
Harmonic Oscillator and Vibrational Spectroscopy



We have confidence that the human spirit will always be able to create ideas fitting somehow to the external objects that are conveyed to us . . .

— Wolfgang Pauli

Abstract This chapter describes the solution of the time independent Schrödinger equation of a harmonic oscillator and shows how the requirement of physically well-behaving eigenfunction leads to the quantization of the harmonic oscillator energy. The solution and its properties are then used for a quantum mechanical description of vibrational states of a diatomic molecule that can be represented by a harmonic oscillator Hamiltonian with reduced mass. Infrared absorption and Raman spectroscopies are introduced, and their selection rules for the case of diatomic molecules are explained. A brief account of how the effects going beyond the harmonic oscillator model for diatomic molecule is provided.

The harmonic oscillator is one of the simplest but the most widely used models in physics, chemistry, and engineering. An analytical solution of the Schrödinger equation for the harmonic oscillator is well known and is described in this chapter. Details of a harmonic oscillator system also clarify important features of quantum mechanical states and energies distinct from those of classical mechanics. Solutions of the quantum harmonic oscillator have contributed immensely to understanding molecular vibrations and a correct quantum mechanical interpretation of spectroscopic data.

3.1 Classical Harmonic Oscillator and Hamiltonian

Let us consider a classical harmonic oscillator with mass m, as illustrated in Fig. 3.1, with l_0 as the equilibrium length of the spring at which there is zero restoring force. The position of the oscillator is defined as the displacement of the oscillator relative

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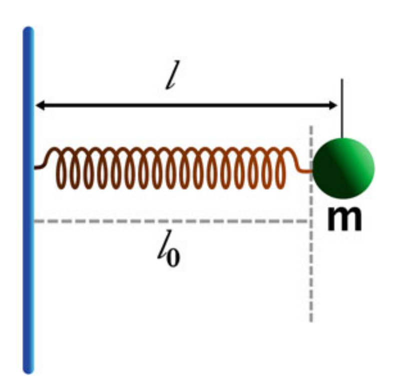


Fig. 3.1 Illustration of a mass m attached to a wall of infinite mass via an ideal massless spring with linear restoring force

to the equilibrium length, namely, $x = l - l_0$. The force applied to the particle at x is then given by

$$F(x) = -k(l - l_0) = -kx, \tag{3.1}$$

where k is the spring constant. The Newtonian equation for the mass attached to the spring is then equal to

$$m\frac{d^2}{dt^2}x(t) = -kx(t) = -m\omega^2 x(t), \tag{3.2}$$

where $\omega = \sqrt{k/m}$. It is straightforward to show that the solution of the above equation is

$$x(t) = x(0)\cos(\omega t) + \frac{p(0)}{m\omega}\sin(\omega t), \tag{3.3}$$

where $x(0)$ and $p(0)$ are position and momentum at time $t = 0$. The classical momentum of the particle can be calculated by taking the time derivative of the above expression as follows:

$$p(t) = m\frac{d}{dt}x(t) = p(0)\cos(\omega t) - m\omega x(0)\sin(\omega t). \tag{3.4}$$

On the other hand, the Hamiltonian of the harmonic oscillator is

$$H = \frac{p^2}{2m} + \frac{m\omega^2}{2}x^2, \tag{3.5}$$

where the second term is the potential energy of the harmonic oscillator at x. It is straightforward to show that the time dependent position and momentum given by Eqs. (3.3) and (3.4) conserve the above Hamiltonian.

Now, let us assume that the particle no longer behaves classically but should be considered as a quantum mechanical particle. Then, determining the position and momentum of the particle both *simultaneously and precisely* has no physical meaning in quantum mechanics. As yet, the expression for the Hamiltonian, Eq. (3.5), remains valid except that the position and momentum be replaced with operators as follows:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2. \tag{3.6}$$

Solving the time independent Schrödinger equation for the above Hamiltonian is the first step for understanding how the quantum harmonic oscillator can be described and probed. This is also essential for correct quantum mechanical understanding of molecular vibrations.

3.2 Schrödinger Equation

The time independent Schrödinger equation (in the Dirac notation) for the harmonic oscillator Hamiltonian, Eq. (3.6), is

$$\hat{H}|\psi\rangle = \left(\frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2\right)|\psi\rangle = E|\psi\rangle. \tag{3.7}$$

Taking the inner product of the above equation with the position state bra $\langle x|$, we obtain

$$\begin{aligned}\langle x|\hat{H}|\psi\rangle &= \langle x|\left(\frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2\right)|\psi\rangle \\ &= \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{m\omega^2}{2}x^2\right)\langle x|\psi\rangle = E\langle x|\psi\rangle. \end{aligned} \tag{3.8}$$

The second line in the above equation corresponds to the original Schrödinger equation because $\langle x|\psi\rangle = \psi(x)$. The Schrödinger equation for this wavefunction can be expressed as

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \left(E - \frac{m\omega^2}{2}x^2\right)\psi(x) = 0, \tag{3.9}$$

where we have moved all the terms to the lefthand side and changed the sign so that the second derivative becomes positive. Detailed mathematical steps for solving this differential equation are provided below.

3.2.1 Solution of Time Independent Schrödinger Equation

As the first step for solving Eq. (3.9), let us introduce a new scaled coordinate $\xi = \sqrt{\gamma}x$, where γ is yet unknown real parameter with a unit of inverse length square, and also define $\phi(\xi) = \psi(x)$. Then, $d\xi = \sqrt{\gamma}dx$ and

$$\frac{d^2}{dx^2}\psi(x) = \gamma \frac{d^2}{d\xi^2}\phi(\xi). \tag{3.10}$$

Employing the above relationship in Eq. (3.9), one can obtain the following equation:

$$\frac{\hbar^2\gamma}{2m}\frac{d^2\phi(\xi)}{d\xi^2} + \left(E - \frac{m\omega^2}{2\gamma}\xi^2\right)\phi(\xi) = 0. \tag{3.11}$$

Dividing the above equation with $\hbar^2\gamma/(2m)$, we obtain

$$\frac{d^2\phi(\xi)}{d\xi^2} + \left(\frac{2mE}{\hbar^2\gamma} - \frac{m^2\omega^2}{\hbar^2\gamma^2}\xi^2\right)\phi(\xi) = 0. \tag{3.12}$$

The above equation has two parameters within the parenthesis, one as a constant and the other as a coefficient of ξ^2. Now, the free parameter γ can be determined to remove the second one. Namely, by choosing $\gamma = m\omega/\hbar$, the above equation can be simplified as follows:

$$\frac{d^2\phi(\xi)}{d\xi^2} + (\kappa - \xi^2)\phi(\xi) = 0, \tag{3.13}$$

where

$$\kappa = \frac{2mE}{\hbar^2\gamma} = \frac{2E}{\hbar\omega}. \tag{3.14}$$

While Eq. (3.13) appears to be simple, its conventional solution as a power series expansion of $\phi(\xi)$ with respect to ξ is not straightforward because the resulting equation involves three different powers of ξ. A well-known technique to overcome this difficulty is to factor out a term that dominates for large ξ limit, which then helps identifying an equation that results in a simpler relationship involving only two powers of ξ.

Inspection of Eq. (3.13) shows that the term $-\xi^2\phi(\xi)$ becomes one of dominant terms in the large ξ limit. For this term to be cancelled by the second derivative term, $\phi(\xi)$ should have a term that contains $e^{-\xi^2/2}$ that produces a term with ξ^2 as

a multiplicative factor when second derivative is taken. Thus, let us introduce a new function $H(\xi)$ such that

$$\phi(\xi) = e^{-\xi^2/2} H(\xi). \tag{3.15}$$

Then,

$$\frac{d}{d\xi}\phi(\xi) = -\xi e^{-\xi^2/2} H(\xi) + e^{-\xi^2/2} H'(\xi), \tag{3.16}$$

$$\begin{aligned}\frac{d^2}{d\xi^2}\phi(\xi) &= -e^{-\xi^2/2} H(\xi) + \xi^2 e^{-\xi^2/2} H(\xi) - 2\xi e^{-\xi^2/2} \frac{d}{d\xi} H(\xi) + e^{-\xi^2/2} \frac{d^2}{d\xi^2} H(\xi) \\ &= (\xi^2 - 1)\phi(\xi) - 2\xi e^{-\xi^2/2} \frac{d}{d\xi} H(\xi) + e^{-\xi^2/2} \frac{d^2}{d\xi^2} H(\xi).\end{aligned} \tag{3.17}$$

Inserting the above expression into Eq. (3.13), we obtain

$$\begin{aligned}&\frac{d^2}{d\xi^2}\phi(\xi) + (\kappa - \xi^2)\phi(\xi) \\ &= (\kappa - 1) e^{-\xi^2/2} H(\xi) - 2\xi e^{-\xi^2/2} \frac{dH(\xi)}{d\xi} + e^{-\xi^2/2} \frac{d^2}{d\xi^2} H(\xi) \\ &= e^{-\xi^2/2} \left\{ \frac{d^2}{d\xi^2} H(\xi) - 2\xi \frac{d}{d\xi} H(\xi) + (\kappa - 1) H(\xi) \right\} = 0.\end{aligned} \tag{3.18}$$

Since $e^{-\xi^2/2}$ is nonzero, the above equation implies that

$$\frac{d^2}{d\xi^2} H(\xi) - 2\xi \frac{d}{d\xi} H(\xi) + (\kappa - 1) H(\xi) = 0. \tag{3.19}$$

While the above differential equation has an additional term involving the first derivative, it has the same order as the original function $H(\xi)$ because of the additional multiplicative factor ξ. Thus, when a power series solution is assumed for $H(\xi)$, a simple recursion relationship involving terms with only two different powers of ξ appears.

Indeed, Eq. (3.19) is a well-known differential equation called the Hermite equation. The solution of this equation and the condition for κ that allows well-behaving solution can be found as described below. Let us assume the following power series expansion for $H(\xi)$:

$$H(\xi) = C_0 + C_1\xi + C_2\xi^2 + \cdots + C_n\xi^n + C_{n+1}\xi^{n+1} + C_{n+2}\xi^{n+2} + \ldots \tag{3.20}$$

Taking the first and second derivatives of the above expression, we find that

$$\frac{d}{d\xi}H(\xi) = C_1 + 2C_2\xi + \cdots + nC_n\xi^{n-1}$$
$$+(n+1)C_{n+1}\xi^n + (n+2)C_{n+2}\xi^{n+1} + \ldots, \tag{3.21}$$
$$\frac{d^2}{d\xi^2}H(\xi) = 2C_2 + \cdots + n(n-1)C_n\xi^{n-2}$$
$$+(n+1)nC_{n+1}\xi^{n-1} + (n+2)(n+1)C_{n+2}\xi^n + \ldots. \tag{3.22}$$

Inserting Eqs. (3.20)–(3.22) into Eq. (3.19) and requiring that the coefficient of each term ξ^n is zero lead to the following relation between coefficients:

$$(n+2)(n+1)C_{n+2} - 2nC_n + (\kappa - 1)C_n = 0. \tag{3.23}$$

Solving the above equation with respect to C_{n+2}, we obtain the following recursion relationship:

$$C_{n+2} = \frac{2n - \kappa + 1}{(n+2)(n+1)}C_n. \tag{3.24}$$

It is easy to find that the above recursion relationship implies that C_{n+2} should be zero for some finite n in order for the wave function to be physically acceptable. This can be shown as follows.

For simplicity, let us assume that $C_1 = 0$. Then, we only need to consider even terms. For large $n = 2n' >> (\kappa - 1)/2$ & 1, Eq. (3.24) approximately becomes

$$C_{2(n'+1)} \approx \frac{4n'}{2(n'+1)2n'}C_{2n'}. \tag{3.25}$$

The above relation implies that $C_{2n'} \approx C_0/n'!$ for large n'. In this case, $H(\xi) \sim C_0 e^{\xi^2}$ for large ξ. When this expression is used in Eq. (3.15), the resulting wavefunction behaves as follows:

$$\phi(\xi) \sim C_0 e^{-\xi^2/2} e^{\xi^2} = C_0 e^{\xi^2/2} \text{ as } \xi \to \infty. \tag{3.26}$$

For nonzero C_1, following a similar reasoning, the function can be shown to contain a term that behaves as $C_1 \xi e^{\xi^2/2}$ for large ξ as well.

The asymptotic behavior of Eq. (3.26) shows that $\phi(\xi)$ is not an acceptable solution, if the series for $H(\xi)$ continue up to an infinite order, because it means that the probability to find the position to be at infinity is infinitely large, which is unphysical. The only way out of this is for the series Eq. (3.20) to terminate at finite order. Then, $H(\xi)$ becomes a polynomial and $\phi(\xi) = H(\xi)e^{-\xi^2/2}$ becomes zero for

$\xi \to \infty$. Inspection of Eq. (3.24) shows that the termination of the series is possible if the following condition is satisfied.

$$\kappa = 2v + 1, v = 0, 1, \ldots \tag{3.27}$$

Employing the definition of κ given by Eq. (3.14), we find that the above condition implies that the energy should have the following form:

$$E_v = \hbar\omega \left(v + \frac{1}{2} \right) , v = 0, 1, \ldots \tag{3.28}$$

The corresponding solution for each v, $H_v(\xi)$, is called a Hermite polynomial, which is a polynomial of ξ with maximum power of v.

Since the recursion relationship, Eq. (3.24), involves terms with two order difference in ξ, solutions should consist of terms with even or odd powers of ξ depending on the value of v. That is, for even v, solution for Eq. (3.24) exists only for $C_1 = 0$. For odd v, the solution exists only for $C_0 = 0$. Examples of these polynomials, known as Hermite polynomials, and a few terms for general expressions are provided in Table 3.1.

On the other hand, it is also known that the above Hermite polynomials can be generated from a Gaussian-type function as follows:

$$e^{-s^2+2s\xi} = \sum_{v=0}^{\infty} \frac{1}{v!} H_v(\xi) s^v, \tag{3.29}$$

where the left hand side is called the generating function of the Hermite polynomial.

Summing up the results obtained so far, the eigenfunction for each energy E_v can be expressed as

$$\psi_v(x) = N_v e^{-\gamma x^2/2} H_v(\sqrt{\gamma} x), \tag{3.30}$$

Table 3.1 Examples of Hermite polynomials and general expressions. Note that the second and third terms are shown assuming that $m \geq 4$. For $m = 1$, only the first and the last terms exist. For $m = 2$, only the first, second, and last terms exist

n	$H_n(\xi)$
0	1
1	2ξ
2	$4\xi^2 - 2$
3	$8\xi^3 - 12\xi$
4	$16\xi^4 - 48\xi^2 + 12$
5	$32\xi^5 - 160\xi^3 + 120\xi$
6	$64\xi^6 - 480\xi^4 + 720\xi^2 - 120$
$2m$	$(2\xi)^{2m} - \frac{(2m)!}{(2m-2)!2!}(2\xi)^{2m-2} + \frac{(2m)!}{(2m-4)!4!}(2\xi)^{2m-4} + \cdots + (-1)^m \frac{(2m)!}{m!}$
$2m + 1$	$(2\xi)^{2m+1} - \frac{(2m+1)!}{(2m-1)!2!}(2\xi)^{2m-1} + \frac{(2m+1)!}{(2m-3)!4!}(2\xi)^{2m-3} + \cdots + (-1)^m \frac{(2m+1)!}{m!}(2\xi)$

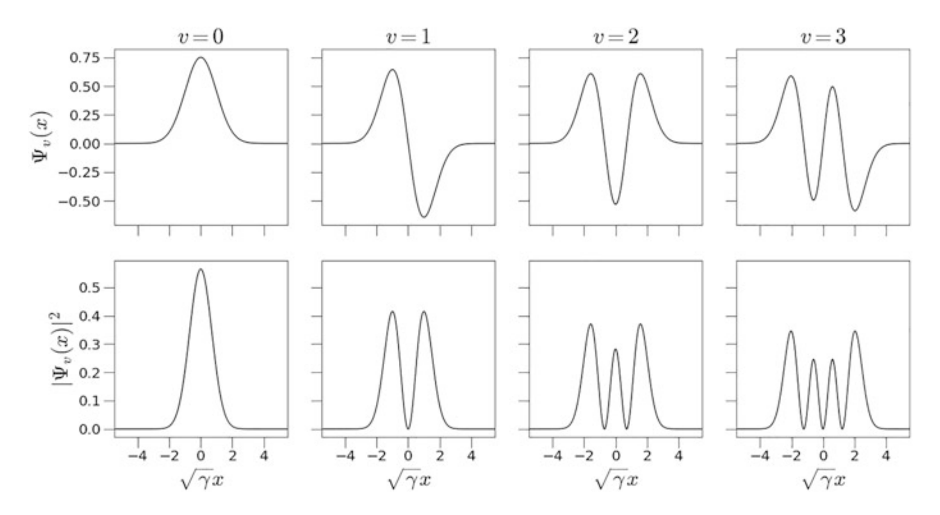


Fig. 3.2 Four eigenfunctions $\psi_v(x)$'s with $v = 0, 1, 2,$ and 3 and corresponding probability densities, $|\psi_v(x)|^2$, for a harmonic oscillator

where N_v is the normalization constant and can be determined by the following normalization condition:

$$\int_{-\infty}^{\infty} \psi_v(x)^2 dx = N_v^2 \int_{-\infty}^{\infty} e^{-\gamma x^2} H_v(\sqrt{\gamma}x)^2 dx = 1. \tag{3.31}$$

The integration over the Hermite polynomial in the above equation can be done explicitly, which leads to the following expression:

$$N_v = \frac{1}{\sqrt{2^v v!}} \left(\frac{\gamma}{\pi}\right)^{1/4}, \tag{3.32}$$

where note that $0! = 1$. Figure 3.2 shows $\psi_v(x)$ for $v = 0, \cdots, 3$ and the corresponding probability densities.

There are three properties of Hermite polynomials that are important for harmonic oscillators as described below.

Properties of Hermite Polynomials

- Orthogonality and normalization condition

$$\int_{-\infty}^{\infty} d\xi\, H_v(\xi) H_{v'}(\xi) e^{-\xi^2} = \delta_{vv'} \frac{\sqrt{\gamma}}{N_v^2}, \tag{3.33}$$

(continued)

where N_v is the normalization constant defined by Eq. (3.32). Also, note that $\xi = \sqrt{\gamma}x$. For $v \neq v'$, the above equation amounts to the orthogonality condition for the eigenfunctions of the harmonic oscillator.

- Recursion relationship involving three consecutive Hermite polynomials:

$$H_{v+1}(\xi) - 2\xi H_v(\xi) + 2v H_{v-1}(\xi) = 0. \tag{3.34}$$

The above relationship allows generating all the higher order Hermite polynomials from $H_0(\xi)$ and $H_1(\xi)$.

- Relationship involving the derivative of a Hermite polynomial:

$$\frac{d}{d\xi}H_v(\xi) = 2v H_{v-1}(\xi). \tag{3.35}$$

The combination of Eqs. (3.33) and (3.34) for $v' = v \pm 1$ can be used to show that

$$\langle \hat{x} \rangle_v = \int_{-\infty}^{\infty} dx \psi_v(x) x \psi_v(x) = 0. \tag{3.36}$$

The combination of Eqs. (3.33)–(3.35) can be used to show that

$$\langle \hat{p} \rangle_v = \frac{\hbar}{i} \int_{-\infty}^{\infty} dx \psi_v(x) \frac{\partial}{\partial x} \psi_v(x) = 0. \tag{3.37}$$

The recursion relationship, Eq. (3.34), can also be used for evaluating the following expectation value of $\hat{x}^2$ with respect to the vth eigenstate.

$$\langle \hat{x}^2 \rangle_v = \int_{-\infty}^{\infty} dx \psi_v^*(x) x^2 \psi_v(x) = N_v^2 \frac{1}{\sqrt{\gamma}} \frac{1}{\gamma} \int_{-\infty}^{\infty} d\xi \, H_v^2(\xi) \xi^2 e^{-\xi^2}. \tag{3.38}$$

In the above expression, Eq. (3.34) can be used twice as follows:

$$\begin{aligned} \xi^2 H_v(\xi) &= \xi \left(\frac{1}{2} H_{v+1}(\xi) + v H_{v-1}(\xi) \right) \\ &= \frac{1}{4} H_{v+2}(\xi) + \frac{1}{2}(v+1) H_v(\xi) + \frac{v}{2} H_v(\xi) + v(v-1) H_{v-2}(\xi). \end{aligned} \tag{3.39}$$

When this expression is inserted into Eq. (3.38), the integrations involving products of $H_{v+2}(\xi)$ and $H_{v-2}(\xi)$ with $H_v(\xi)$ vanish due to the orthogonality condition, and only the term involving $H_v^2(\xi)$ survives. Thus,

$$\begin{aligned}\langle\hat{x}^2\rangle_v &= N_v^2\frac{1}{\gamma^{3/2}}\frac{(2v+1)}{2}\int_{-\infty}^{\infty}d\xi\, H_v^2(\xi)e^{-\xi^2}\\ &= N_v^2\frac{1}{\gamma^{3/2}}\frac{(2v+1)}{2}\frac{\sqrt{\gamma}}{N_v^2}=\frac{(2v+1)}{2\gamma}\\ &= \frac{\hbar}{m\omega}\left(v+\frac{1}{2}\right).\end{aligned} \tag{3.40}$$

Since

$$\langle\hat{H}\rangle_v=\frac{1}{2m}\langle\hat{p}^2\rangle_v+\frac{1}{2}m\omega^2\langle\hat{x}^2\rangle_v=\hbar\omega\left(v+\frac{1}{2}\right), \tag{3.41}$$

Eq. (3.40) implies that

$$\langle\hat{p}^2\rangle_v=2m\frac{\hbar\omega}{2}\left(v+\frac{1}{2}\right)=m\hbar\omega\left(v+\frac{1}{2}\right). \tag{3.42}$$

From Eqs. (3.36), (3.37), (3.40), and (3.42), it is easy to show that the position and the momentum have the following magnitudes of uncertainties for the ground vibrational state:

$$\sigma_x=\left(\langle\hat{x}^2\rangle_0-\langle\hat{x}\rangle_0^2\right)^{1/2}=\left(\langle\hat{x}^2\rangle_0\right)^{1/2}=\sqrt{\frac{\hbar}{2m\omega}}, \tag{3.43}$$

$$\sigma_p=\left(\langle\hat{p}^2\rangle_0-\langle\hat{p}\rangle_0^2\right)^{1/2}=\left(\langle\hat{p}^2\rangle_0\right)^{1/2}=\sqrt{\frac{m\hbar\omega}{2}}. \tag{3.44}$$

Thus,

$$\sigma_x\sigma_p=\frac{\hbar}{2}. \tag{3.45}$$

This means that the ground vibrational eigenstate is the minimum uncertainty state.

The recursion relationship, Eq. (3.34), can also be used for calculating the following quantity:

$$\begin{aligned}\int_{-\infty}^{\infty}dx\ \psi_v(x)x\psi_{v'}(x) &= N_vN_{v'}\frac{1}{\gamma}\int_{-\infty}^{\infty}d\xi\ H_v(\xi)\xi H_{v'}(\xi)e^{-\xi^2}\\ &= N_vN_{v'}\frac{1}{\gamma}\int_{-\infty}^{\infty}d\xi\left(vH_{v-1}(\xi)+\frac{1}{2}H_{v+1}(\xi)\right)H_{v'}(\xi)e^{-\xi^2}\\ &= N_vN_{v'}\frac{1}{\gamma}\left(v\delta_{v-1v'}\frac{\sqrt{\gamma}}{N_v'^2}+\frac{1}{2}\delta_{v+1v'}\frac{\sqrt{\gamma}}{N_v'^2}\right).\end{aligned} \tag{3.46}$$

Note that Eq. (3.36) is the special case of the above identity for $v = v'$. The above identity implies that the measurement of $\hat{x}$ causes the transition of vibrational state from v to $v \pm 1$. This fact has important implications for the selection rule of the spectroscopy detecting molecular vibrational states.

3.2.2 *Operator Approach*

The commutator between the Hamiltonian, Eq. (3.6), and the position operator is given by

$$[\hat{H}, \hat{x}] = \frac{1}{2m}[\hat{p}^2, \hat{x}] = \frac{1}{2m}\left(\hat{p}[\hat{p}, x] + [\hat{p}, \hat{x}]\hat{p}\right) = -\frac{i\hbar}{m}\hat{p}. \tag{3.47}$$

Similarly,

$$[\hat{H}, \hat{p}] = \frac{m\omega^2}{2}[\hat{x}^2, \hat{p}] = \frac{m\omega^2}{2}\left(\hat{x}[\hat{x}, \hat{p}] + [\hat{x}, \hat{p}]\hat{x}\right) = i\hbar m\omega^2\hat{x}. \tag{3.48}$$

Combining Eqs. (3.47) and (3.48), we find that

$$[\hat{H}, m\omega\hat{x} + i\hat{p}] = -i\hbar\omega\hat{p} - \hbar m\omega^2\hat{x} = -\hbar\omega(m\omega\hat{x} + i\hat{p}), \tag{3.49}$$

$$[\hat{H}, m\omega\hat{x} - i\hat{p}] = -i\hbar\omega\hat{p} + \hbar m\omega^2\hat{x} = \hbar\omega(m\omega\hat{x} - i\hat{p}). \tag{3.50}$$

The above identities motivate definition of two important operators as described below.

Definition 3.1 For the harmonic oscillator with mass m and angular frequency ω, its lowering and raising operators $\hat{b}$ and $\hat{b}^\dagger$ are defined as follows:

$$\hat{b} = \frac{1}{\sqrt{2m\hbar\omega}}(m\omega\hat{x} + i\hat{p}) = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + i\frac{\hat{p}}{\sqrt{2m\hbar\omega}}, \tag{3.51}$$

$$\hat{b}^\dagger = \frac{1}{\sqrt{2m\hbar\omega}}(m\omega\hat{x} - i\hat{p}) = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - i\frac{\hat{p}}{\sqrt{2m\hbar\omega}}. \tag{3.52}$$

The lowering and raising operators defined above have the following important properties.

Properties of Lowering and Raising Operators

- Raising and lowering operators satisfy the following commutation relations:

$$[\hat{H}, \hat{b}] = -\hbar\omega\hat{b}, \tag{3.53}$$

$$[\hat{H}, \hat{b}^\dagger] = \hbar\omega\hat{b}^\dagger, \tag{3.54}$$

$$[\hat{b}, \hat{b}^\dagger] = 1. \tag{3.55}$$

- The product of $\hat{b}^\dagger$ and $\hat{b}$ can be shown to be

$$\begin{aligned}\hat{b}^\dagger\hat{b} &= \left(\sqrt{\frac{m\omega}{2\hbar}}\hat{x} - i\frac{\hat{p}}{\sqrt{2m\hbar\omega}}\right)\left(\sqrt{\frac{m\omega}{2\hbar}}\hat{x} + i\frac{\hat{p}}{\sqrt{2m\hbar\omega}}\right),\\ &= \frac{m\omega}{2\hbar}\hat{x}^2 + \frac{i}{2\hbar}\hat{x}\hat{p} - \frac{i}{2\hbar}\hat{p}\hat{x} + \frac{\hat{p}^2}{2m\hbar\omega} = \frac{1}{\hbar\omega}\hat{H} - \frac{1}{2}.\end{aligned} \tag{3.56}$$

Therefore,

$$\hat{H} = \hbar\omega\left(\hat{b}^\dagger\hat{b} + \frac{1}{2}\right). \tag{3.57}$$

Equation (3.57) is equivalent to Eq. (3.6), and offers an efficient way to obtain some of the key properties of the quantum harmonic oscillator. As will be shown below, this expression allows to deduce the details of how the eigenvalues are quantized even without solving the Schrödinger equation.

For now, let us assume that we have no knowledge of the solution of the Schrödinger equation in the previous subsection. Thus, let us suppose an eigenstate of the Hamiltonian $|E\rangle$ such that

$$\hat{H}|E\rangle = E|E\rangle, \tag{3.58}$$

where E is as yet unknown value. Then, one can show that $\hat{b}|E\rangle$ and $\hat{b}^\dagger|E\rangle$ are eigenstates of $\hat{H}$ with different eigenvalues using the commutation relations. For example,

$$[\hat{H}, \hat{b}]|E\rangle = \hat{H}(\hat{b}|E\rangle) - \hat{b}(\hat{H}|E\rangle) = -\hbar\omega\hat{b}|E\rangle, \tag{3.59}$$

where Eq. (3.53) has been used. Using the assumption of Eq. (3.58) and sending $\hat{b}\hat{H}|E\rangle = E\hat{b}|E\rangle$ to the righthand side, the above equation implies that

$$\hat{H}(\hat{b}|E\rangle) = (E - \hbar\omega)\hat{b}|E\rangle. \tag{3.60}$$

Thus $\hat{b}|E\rangle$ is an eigenstate of $\hat{H}$ but with an eigenvalue $E - \hbar\omega$, which is lower than the original value by $\hbar\omega$. Similarly, one can show that

$$\hat{H}(\hat{b}^{\dagger}|E\rangle) = (E + \hbar\omega)\hat{b}^{\dagger}|E\rangle. \quad (3.61)$$

Thus, $\hat{b}^{\dagger}$ is an eigenstate of $\hat{H}$ but with a different eigenvalue $E + \hbar\omega$, which is higher than the original value by $\hbar\omega$.

The Hamiltonian of the harmonic oscillator is positive definite. Therefore,

$$\langle E|\hat{H}|E\rangle = E \geq 0. \quad (3.62)$$

Let us denote the lowest energy state as $|E_0\rangle$. Then, it is clear that $\hat{b}|E_0\rangle = 0$. If this is not the case, $\hat{b}|E_0\rangle$ becomes an eigenstate of $\hat{H}$ with eigenvalue of $E_0 - \hbar\omega$, which contradicts the assumption that E_0 is the lowest possible value. This in turn implies that

$$\hat{H}|E_0\rangle = \hbar\omega(\hat{b}^{\dagger}\hat{b} + \frac{1}{2})|E_0\rangle = \frac{\hbar\omega}{2}|E_0\rangle. \quad (3.63)$$

Therefore,

$$E_0 = \frac{\hbar\omega}{2}. \quad (3.64)$$

Now, let us denote $|E_0\rangle$ as $|0\rangle$ and assume that it is normalized. Then, we can generate eigenstates with eigenvalues $\hbar\omega(v + 1/2)$ by applying $\hat{b}^{\dagger}$ on $|0\rangle$ by v times repeatedly. Let us denote the normalized eigenstates generated in such a way as $|v\rangle$. In other words,

$$\hat{b}^{\dagger}|v\rangle = A_v|v + 1\rangle, \;\; v = 0, 1, 2, \cdots, \quad (3.65)$$

where we have introduced a constant factor A_v because $\hat{b}^{\dagger}$ does not conserve normalization. This can be shown by taking inner product of $\hat{b}^{\dagger}|v\rangle$ with itself as follows:

$$\left(\langle v|\hat{b}\right)\left(\hat{b}^{\dagger}|v\rangle\right) = \langle v|\left(\frac{\hat{H}}{\hbar\omega} + \frac{1}{2}\right)|v\rangle = v + 1 = |A_v|^2, \quad (3.66)$$

where Eqs. (3.55) and (3.56) were used in the first equality, and the fact that $\hat{H}|v\rangle = \hbar\omega(v + 1/2)$ was used in the second equality. The last equality is from Eq. (3.65) along with the fact that $|v\rangle$ is normalized. Therefore, we find that

$$\hat{b}^{\dagger}|v\rangle = \sqrt{v + 1}|v + 1\rangle. \quad (3.67)$$

This implies that the vth eigenstate can be defined as

$$|v\rangle = \frac{1}{\sqrt{v!}}(\hat{b}^\dagger)^v|0\rangle, \tag{3.68}$$

where $|v\rangle$ is normalized and

$$\hat{H}|v\rangle = \hbar\omega(v + \frac{1}{2})|v\rangle. \tag{3.69}$$

Note that the above equation is nothing but the time independent Schrödinger equation for the eigenvalue, Eq. (3.28). It is remarkable that this result can be obtained purely out of the commutator relationship between $\hat{H}$, $\hat{b}$, and $\hat{b}^\dagger$ and that there has to be a lower bound in the eigenvalue.

In a similar manner to obtaining Eq. (3.67), we can obtain the following identity involving the operation of $\hat{b}$.

$$\hat{b}|v\rangle = \sqrt{v}|v-1\rangle, \; v = 1, 2, 3, \ldots . \tag{3.70}$$

This identity can be used to confirm that the eigenvalues $\hbar\omega(v + 1/2)$'s are the only eigenvalues possible for the harmonic oscillator.

3.2.3 General Time Dependent State

A general (normalized) quantum mechanical state for a harmonic oscillator can be expressed as

$$|\psi\rangle = \sum_v C_v|v\rangle, \tag{3.71}$$

where $\sum_v |C_v|^2 = 1$. The corresponding wavefunction (position representation) is given by

$$\psi(x) = \langle x|\psi\rangle = \sum_v C_v\langle x|v\rangle = \sum_v C_v\psi_v(x). \tag{3.72}$$

The normalization condition for $|v\rangle$ is as follows:

$$\begin{aligned}
\langle v|v'\rangle &= \langle v|\hat{1}|v'\rangle = \int_{-\infty}^{\infty} dx \langle v|x\rangle\langle x|v'\rangle \\
&= \frac{1}{\sqrt{2^v v!}}\frac{1}{\sqrt{2^{v'}v'!}}\left(\frac{\gamma}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} dx\, e^{-\gamma x^2} H_v(\sqrt{\gamma}x)H_{v'}(\sqrt{\gamma}x) \\
&= \delta_{vv'},
\end{aligned} \tag{3.73}$$

which can be proved employing the property of the Hermite polynomial.

Let us assume that the quantum mechanical state at $t = 0$ is given by

$$|\psi; t = 0\rangle = \sum_v C_v |v\rangle. \tag{3.74}$$

Then, the state at time t is given by

$$|\psi; t\rangle = \sum_v C_v e^{-iE_v t/\hbar} |v\rangle = \sum_v C_v e^{-i\omega(v+1/2)t} |v\rangle. \tag{3.75}$$

Taking time derivative of the above expression, we find that the state indeed satisfies the time dependent Schrödinger equation as shown below.

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} |\psi; t\rangle &= \sum_v C_v \hbar\omega \left(v + \frac{1}{2}\right) e^{-i\omega(v+\frac{1}{2})t} |v\rangle \\ &= \sum_v C_v \hat{H} e^{-i\omega(v+\frac{1}{2})t} |v\rangle \\ &= \hat{H} |\psi; t\rangle. \end{aligned} \tag{3.76}$$

3.3 Vibrational Spectroscopy of Diatomic Molecules

Let us consider a diatomic molecule consisting of two atomic masses m_1 and m_2. At the simplest level, their bonding can be modeled by an ideal spring with spring constant k. If we denote the two coordinates along the internuclear axis as l_1 and l_2 (see Fig. 3.3) and assume that their dynamics are governed by the classical mechanics, we arrive at the following equations of motion:

$$\frac{d^2}{dt^2} l_1 = -\frac{k}{m_1}(r_0 - l_2 + l_1), \tag{3.77}$$

$$\frac{d^2}{dt^2} l_2 = -\frac{k}{m_2}(l_2 - l_1 - r_0). \tag{3.78}$$

In above equations, r_0 is the equilibrium bond distance where there is no restoring force of the spring. From the difference of the above two equations, one can obtain the following equation of motion for $l = l_2 - l_1$:

$$\frac{d^2}{dt^2} l = -k \frac{m_1 + m_2}{m_1 m_2} (l - r_0). \tag{3.79}$$

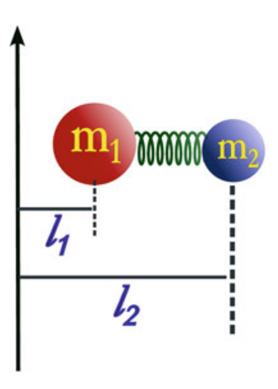


Fig. 3.3 Illustration of two masses m_1 and m_2 connected by an ideal massless spring with linear restoring force

Let us introduce the displacement from the equilibrium bond distance, $x = l - r_0$, and a reduced mass $\mu = m_1 m_2/(m_1 + m_2)$. Then, the above equation simplifies to

$$\frac{d^2}{dt^2}x = -\frac{k}{\mu}x = -\omega^2 x, \tag{3.80}$$

where $\omega = \sqrt{k/\mu}$. Thus, within the classical mechanics, the dynamics of x is equivalent to that of a harmonic oscillator with an effective mass μ, for which the classical Hamiltonian is given by

$$H = \frac{p^2}{2\mu} + \frac{\mu\omega^2}{2}x^2. \tag{3.81}$$

If the above assumption of the classical mechanics were true, it means that the displacement $x(t)$ and its momentum $p(t) = \mu dx(t)/dt$ should go through the following harmonic time evolution

$$x(t) = x(0)\cos(\omega t) + \frac{p(0)}{\mu\omega}\sin(\omega t), \tag{3.82}$$

$$p(t) = p(0)\cos(\omega t) - \mu\omega x(0)\sin(\omega t), \tag{3.83}$$

for which the Hamiltonian $H = p(0)^2/(2\mu) + \mu\omega^2 x(0)^2/2$ remains conserved and can have an arbitrary value depending only on the initial value of the displacement and the momentum.

Quantum mechanically, one has to consider the following Hamiltonian operator corresponding to Eq. (3.81):

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \frac{1}{2}\mu\omega^2\hat{x}^2, \tag{3.84}$$

where $\hat{x}$ and $\hat{p}$ are now operators that should obey the commutator relationship $[\hat{x}, \hat{p}] = i\hbar$. The solution for the Schrödinger equation for the above Hamiltonian is the same as the one presented in Sect. 3.2 except that

$$\gamma = \frac{\mu\omega}{\hbar}, \tag{3.85}$$

for the present case. Thus, the expressions for the eigenvalue, Eq. (3.28), and the eigenfunction, Eq. (3.30), remain the same.

One of the important consequences is that the minimum vibrational energy of the diatomic molecule is no longer zero but becomes $\hbar\omega/2 = \hbar\sqrt{k/\mu}/2$. This also means that the internuclear distance and the corresponding momentum can never become zero simultaneously. For the ground vibrational state, the uncertainties of relative position and momentum of the two atoms within the diatomic molecules can be calculated to be

$$\sigma_x = \sqrt{\frac{\hbar}{2\mu\omega}}, \tag{3.86}$$

$$\sigma_p = \sqrt{\frac{\mu\hbar\omega}{2}}. \tag{3.87}$$

These satisfy the minimum possible value of the Heisenberg's uncertainty relationship, $\sigma_x\sigma_p = \hbar/2$.

3.3.1 Vibrational Absorption or Infrared (IR) Spectroscopy

The quantum mechanical behavior of interatomic displacement in a diatomic molecule can be confirmed from its interaction with light, viewed as electromagnetic radiation. Detailed mathematical treatment of the interaction will be provided later. For now, it is sufficient to accept that the lowest order interaction of light with the displacement is through the dipole moment of the molecule, which is in general defined as

$$\mathbf{D} = \sum_i q_i \mathbf{r}_i, \tag{3.88}$$

where $\mathbf{r}_i$ is the coordinate of the ith particle constituting the molecule. For the case of vibrational spectroscopy, each $\mathbf{r}_i$ can be viewed as the coordinate of each nuclei and q_i the effective point charge of each nucleus, with the effects of electrons incorporated. For the case of a diatomic molecule with their internuclear coordinate $x + r_0$, the dipole moment operator along the internuclear axis is given by

$$\hat{D} = q(\hat{x} + r_0), \tag{3.89}$$

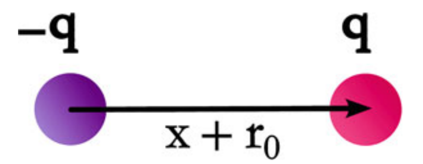


Fig. 3.4 Diatomic molecule and their effective charge and internuclear distance. The arrow represents the dipole moment

where $\hat{x}$ is now viewed as quantum mechanical position operator and q is the magnitude of the effective charge (see Fig. 3.4).

The simplest vibrational spectroscopy is the one where molecular vibrational states changes through the lowest order interaction with light. This is conventionally known as Infrared (IR) spectroscopy because it turns out that the molecular vibrational frequencies are typically in the range of IR. There are two important selection rules as described below.

Selection Rules for IR Spectroscopy

- The first is called gross selection rule stated as follows: *Only vibrational modes that cause change of dipole moment are IR active.* For diatomic molecules, this means that the molecular has to be polar. Therefore, only heteroatomic diatomic molecules are IR active.
- For those molecules that are IR active, the transition that is allowed (given that the harmonic oscillator form of the Hamiltonian is exact) is the following transition:

$$\Delta v = \pm 1. \tag{3.90}$$

  This can be understood from that the IR spectroscopy amounts to applying the dipole operator given by Eq. (3.89) to a given eigenstate, which then makes transition to another eigenstate. Due to the identity of Eq. (3.46), such measurement causes transitions to only nearby eigenstates satisfying Eq. (3.90).

IR spectroscopy is typically an absorption spectroscopy where a photon is absorbed to excite the vibrational state. Thus, within the assumption of the harmonic oscillator model, the energy of the photon being absorbed in the IR spectroscopy is given by

$$h\nu_{ph} = \hbar\omega\left(v + 1 + \frac{1}{2}\right) - \hbar\omega\left(v + \frac{1}{2}\right) = \hbar\omega, \tag{3.91}$$

where ν_{ph} is the frequency of the photon being absorbed and ω is the vibrational angular frequency of the molecule that appears in the Hamiltonian, Eq. (3.84).

The IR spectroscopy is most commonly described in terms of wavenumber, $\tilde{\nu}_{ph} = \nu_{ph}/c$, where c is the speed of light in vacuum. Equation (3.91) can then be expressed in terms of the wavenumber as follows:

$$\tilde{\nu}_{ph} = \frac{\hbar}{2\pi c\hbar}\omega = \frac{1}{2\pi c}\omega = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}. \tag{3.92}$$

For the description of the IR spectroscopy, it is often convenient to introduce the following vibrational term:

$$G(v) = \tilde{\nu}_{vib}\left(v + \frac{1}{2}\right), \tag{3.93}$$

where

$$\tilde{\nu}_{vib} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}. \tag{3.94}$$

Then, the condition for the IR absorption, Eq. (3.92), reduces to

$$\tilde{\nu}_{ph} = \tilde{\nu}_{vib}. \tag{3.95}$$

3.3.2 *Vibrational Raman Spectroscopy*

The next order of interaction between light and molecule is through the polarizability $\boldsymbol{\alpha}$ of the molecule, which is defined by

$$\mathbf{D}_{ind} = \boldsymbol{\alpha}\mathbf{E}. \tag{3.96}$$

This interaction term is quadratic with respect to the amplitude of the field because it involves interaction of the above induced dipole with the electromagnetic field again.

The polarizability $\boldsymbol{\alpha}$ is a matrix in general (second rank tensor) but can be represented by a number for its portion that depends on the vibrational displacement of the diatomic molecule. This can again be expanded with respect to the displacement x as follows:

$$\hat{\alpha} = \alpha(0) + \hat{x}\left.\frac{\partial\alpha}{\partial x}\right|_{x=0} + \cdots. \tag{3.97}$$

This expression shows that the first order interaction term of the molecule with radiation is proportional to the vibrational displacement. This fact leads to the following selection rules for the vibrational Raman spectroscopy.

Selection Rules for Vibrational Raman Spectroscopy

- Any vibrational mode that causes change of polarizability is Raman active. This means that even homonuclear diatomic molecule is in general Raman active because the distance dependence of polarizability is nonzero.
- As in the case of IR spectroscopy, the following selection rule applies to vibrational Raman.

$$\Delta v = \pm 1. \tag{3.98}$$

Unlike the case of IR, Raman Spectroscopy is a scattering process where the frequency difference between in-coming radiation and out-going radiation (in directions perpendicular to in-coming light) is measured. The case where the outgoing light has lower energy corresponds to $\Delta v = 1$ and is called **Stokes vibrational transition**, which is similar to classical inelastic scattering processes that involve loss of energy. The case where the outgoing light has higher energy corresponds to the case of $\Delta v = -1$ and is called **anti-Stokes vibrational transition**, a counter-intuitive process that light extracts energy out of molecules.

3.3.3 Anharmonic Effects

For actual molecules, the potential energy in general deviates from the quadratic dependence as shown in Fig. 3.5. Note that the actual potential energy becomes stiffer (softer) than a quadratic function as the distance becomes smaller (larger). The resulting deviation of the properties of the vibrational motion from those of a harmonic oscillator is called anharmonicity. In general, the potential energy between a diatomic molecule can be expanded as

$$V(x) = V(0) + \frac{m\omega^2}{2}x^2 + \frac{V^{(3)}(0)}{6}x^3 + \frac{V^{(4)}(0)}{24}x^4 + \cdots , \tag{3.99}$$

where $V^{(n)}(0) = \partial^n V(x)/\partial x^n|_{x=0}$. Solving the Schrödinger equation exactly for the general expansion of the potential energy as given above is a difficult task with the exception of few models such as the Morse potential. For the calculation of general anharmonic contributions, one has to rely on approximation methods that you will learn in later chapters of this book, which are valid if the contribution of anharmonic terms are small compared to the harmonic terms.

In actual analyses of spectroscopic data, the following empirical expressions have been frequently used.

$$E_v = \hbar\omega_e\left(v + \frac{1}{2}\right) - x_e\hbar\omega_e\left(v + \frac{1}{2}\right)^2 + y_e\hbar\omega_e\left(v + \frac{1}{2}\right)^3 + \cdots , \tag{3.100}$$

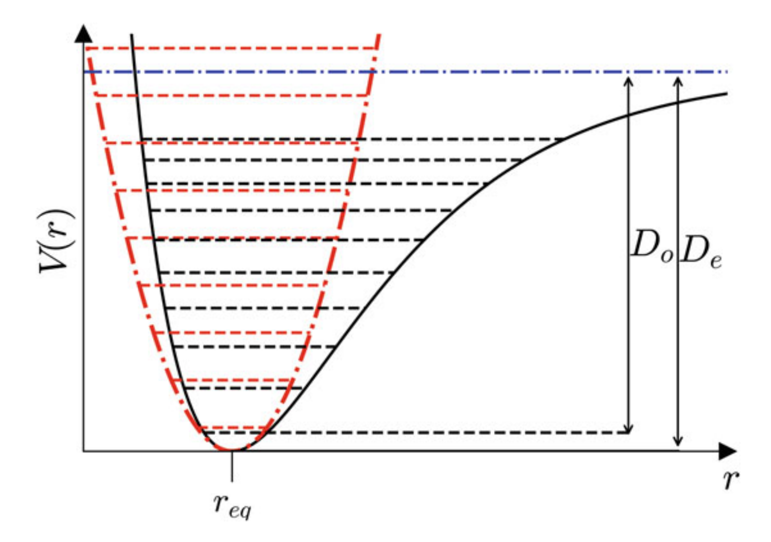


Fig. 3.5 Illustration of a typical diatomic potential energy curve and its parabolic approximation. The quantum energy levels for actual potential and the harmonic oscillator levels for the parabolic approximation are shown. The potential energy depth D_e and the dissociation energy D_0 for actual potential energy are shown as well

where x_e and y_e are called anharmonicity coefficients and are much smaller than one. Or, in terms of vibrational term symbols,

$$G_v = \tilde{\nu}_e\left(v+\frac{1}{2}\right) - x_e\tilde{\nu}_e\left(v+\frac{1}{2}\right)^2 + y_e\tilde{\nu}_e\left(v+\frac{1}{2}\right)^3 + \cdots . \tag{3.101}$$

Two major effects of anharmonicity are (1) non-uniform level spacing and (2) finite dissociation energy (see Fig. 3.5). In general, the potential well-depth is denoted as D_e and the dissociation energy is denoted as D_0. The difference between these two is the zero point energy of the vibrational motion. According to Eq. (3.100), the expression for this is as follows:

$$D_e - D_0 = \frac{1}{2}\hbar\omega_e - \frac{1}{4}x_e\hbar\omega_e + \frac{1}{8}y_e\hbar\omega_e + \cdots , \tag{3.102}$$

In terms of the wavenumber, the above quantity can be expressed as

$$\tilde{D}_e - \tilde{D}_0 = \frac{1}{2}\tilde{\nu}_e - \frac{1}{4}x_e\tilde{\nu}_e + \frac{1}{8}y_e\tilde{\nu}_e + \cdots . \tag{3.103}$$

The above expression shows that the anharmonic effect in general reduces the zero point energy.

3.4 Summary and Questions

The time independent Schrödinger equation for a harmonic oscillator has exact solutions. Eigenvalues of the Hamiltonian are given by Eq. (3.28), which are quantized with an equal spacing. The corresponding eigenfunctions are given by Eq. (3.30), which are given by Hermite polynomials (listed in Table 3.1) multiplied with a common Gaussian function. The quantization of the eigenvalue arises from the requirement that the eigenfunctions remain finite and that its squares are integrable over the entire value of the position. The ground vibrational state of the harmonic oscillator is a minimum uncertainty state that satisfies Eq. (3.45).

By introducing $\hat{b}$ and $\hat{b}^\dagger$, lowering and raising operators that are defined by Eqs. (3.51) and (3.52), one can express the Hamiltonian of the harmonic oscillator in the form of Eq. (3.57). The raising operator, when applied to an eigenstate of the Hamiltonian, produces the next higher eigenstate according to Eq. (3.67). The lowering operator, when applied to an eigenstate of the Hamiltonian, produces the next lower eigenstate according to Eq. (3.70). Application of the lowering operator to the ground vibrational state results in a null state, which means that the state does not exist any more. It is possible to make a complete description of a quantum harmonic oscillator, including the dynamics, solely in terms of expressions involving $\hat{b}$ and $\hat{b}^\dagger$.

The vibrational motion of a diatomic molecule, given that the interatomic potential energy is well approximated by a quadratic function of the relative displacement, can be represented by a harmonic oscillator with a reduce mass μ as defined below Eq. (3.79). Thus, the eigenfunction and eigenvalue of the harmonic oscillator with the reduced mass can be used for quantum mechanical understanding of the molecular vibration and selection rules for IR and Raman spectroscopies as given by Eqs. (3.90) and (3.98). For diatomic molecules with soft potential energy and/or in high vibrational states, the harmonic oscillator assumption breaks down. The resulting anharmonic effects can be effectively represented by the modification of the expression for the vibration energy as in Eq. (3.100), although this expression is empirical.

Questions

- In solving the time independent Schrödinger equation for a harmonic oscillator, which requirement for the wavefunction causes eigenvalues of the Hamiltonian to be quantized?
- The ground vibrational state of a harmonic oscillator is a minimum uncertainty state. Is it the only minimum uncertainty state that can be found for the harmonic oscillator?

(continued)

- Time dependent expectation values for position and momentum operators of a harmonic oscillator appear to satisfy the classical Newtonian equation of motion. What is the reason for this apparent classical behavior?
- How are the expectation values of the kinetic and potential energies of a quantum harmonic oscillator related with each other?
- Are the raising ($\hat{b}^\dagger$) and lowering ($\hat{b}$) operators of a quantum harmonic oscillator physical observables?
- What makes a diatomic molecule IR active and what is the transition being involved in an IR absorption?
- What makes a diatomic molecule Raman active and what transitions are involved in Stokes and anti-Stokes Raman transitions respectively?
- For a given diatomic molecule, how are the dissociation energy, the depth of the potential energy, and the zero point energy of the vibration related?
- If anharmonic effects become significant for the vibration of a diatomic molecule, do the selection rules for IR and Raman transitions, $\Delta v = \pm 1$, still remain the same?

Exercise Problems with Solutions

3.1 Prove that the time dependent position and momentum of the classical harmonic oscillator given by Eqs. (3.3) and (3.4) conserve the classical Hamiltonian, Eq. (3.5).

Solution 3.1 Hamiltonian at time t is shown to be independent of t and the same as that for $t = 0$ as follows.

$$
\begin{aligned}
\frac{p(t)^2}{2m} + \frac{1}{2}m\omega^2 x(t)^2 &= \frac{1}{2m}\Big(p(0)\cos(\omega t) - m\omega x(0)\sin(\omega t)\Big)^2 \\
&\quad + \frac{1}{2}m\omega^2\Big(x(0)\cos(\omega t) + \frac{p(0)}{m\omega}\sin(\omega t)\Big)^2 \\
&= \frac{p(0)^2}{2m}\Big(\cos^2(\omega t) + \sin^2(\omega t)\Big) \\
&\quad + \frac{1}{2}m\omega^2 x(0)^2\Big(\sin^2(\omega t) + \cos^2(\omega t)\Big) \\
&= \frac{p(0)^2}{2m} + \frac{1}{2}m\omega^2 x(0)^2.
\end{aligned}
$$

3.2 Confirm that the recursion relationship, Eq. (3.34), holds true for $v = 1, 2$ using the expressions for the Hermite polynomial provided in Table 3.1.

Solution 3.2 For $v = 1$,

$$\begin{aligned} H_2(\xi) - 2\xi H_1(\xi) + 2H_0(\xi) &= 4\xi^2 - 2 - 2\xi \cdot (2\xi) + 2. \\ &= 4\xi^2 - 2 - 4\xi^2 + 2 = 0. \end{aligned}$$

For $v = 2$,

$$\begin{aligned} H_3(\xi) - 2\xi H_2(\xi) + 4H_1(\xi) &= 8\xi^3 - 12\xi - 2\xi(4\xi^2 - 2) + 4 \cdot 2\xi \\ &= 8\xi^3 - 12\xi - 8\xi^3 + 4\xi + 8\xi = 0. \end{aligned}$$

3.3 Use the recursion relationship, Eq. (3.34), to find out the expression for $H_4(\xi)$ and $H_5(\xi)$ employing the expressions for $H_2(\xi)$ and $H_3(\xi)$ provided in Table 3.1.

Solution 3.3 For $v = 4$,

$$\begin{aligned} H_4(\xi) &= 2\xi H_3(\xi) - 6H_2(\xi) \\ &= 2\xi(8\xi^3 - 12\xi) - 6(4\xi^2 - 2) \\ &= 16\xi^4 - 24\xi^2 - 24\xi^2 + 12 \\ &= 16\xi^4 - 48\xi^2 + 12. \end{aligned}$$

For $v = 5$,

$$\begin{aligned} H_5(\xi) &= 2\xi H_4(\xi) - 8H_3(\xi) \\ &= 2\xi(16\xi^4 - 48\xi^2 + 12) - 8(8\xi^3 - 12\xi) \\ &= 32\xi^5 - 96\xi^3 + 24\xi - 64\xi^3 + 96\xi \\ &= 32\xi^5 - 160\xi^3 + 120\xi. \end{aligned}$$

3.4 Prove that the expectation values of position $\hat{x}$ and momentum $\hat{p}$ for eigenstates of the harmonic oscillator are zero.

Solution 3.4 For the position,

$$\begin{aligned} \langle \hat{x} \rangle &= \int_{-\infty}^{\infty} dx \psi_v(x) x \psi_v(x) \\ &= N_v^2 \int_{-\infty}^{\infty} dx e^{-\gamma x^2} H_v(\sqrt{\gamma} x) x H_v(\sqrt{\gamma} x) \\ &= \frac{N_v^2}{\gamma} \int_{-\infty}^{\infty} d\xi e^{-\xi^2} H_v(\xi) \xi H_v(\xi) \end{aligned}$$

$$= \frac{N_v^2}{\gamma} \int_{-\infty}^{\infty} d\xi e^{-\xi^2} H_v(\xi) \left(\frac{1}{2} H_{v+1}(\xi) + v H_{v-1}(\xi) \right)$$
$$= \frac{N_v^2}{2} \int_{-\infty}^{\infty} e^{-\xi^2} H_v(\xi) H_{v+1}(\xi) + \frac{v}{\gamma} N_v^2 \int_{-\infty}^{\infty} d\xi e^{-\xi^2} H_v(\xi) H_{v-1}(\xi) = 0,$$

where the last equality is due to the orthogonality of different eigenfunctions of the harmonic oscillator. For the momentum,

$$\langle \hat{p} \rangle = \int_{-\infty}^{\infty} dx \psi_v(x) \frac{\hbar}{i} \frac{\partial}{\partial x} \psi_v(x)$$
$$= N_v^2 \int_{-\infty}^{\infty} dx e^{-\gamma x^2/2} H_v(\sqrt{\gamma} x) \frac{\hbar}{i} \frac{\partial}{\partial x} e^{-\gamma x^2/2} H_v(\sqrt{\gamma} x)$$
$$= N_v^2 \frac{\hbar}{i} \int_{-\infty}^{\infty} dx e^{-\gamma x^2/2} H_v(\sqrt{\gamma} x) \Big[-\gamma x e^{-\gamma x^2/2} H_v(\sqrt{\gamma} x)$$
$$+ \sqrt{\gamma} e^{-\gamma x^2/2} H_v'(\sqrt{\gamma} x) \Big].$$

Combining the two $e^{-\gamma x^2/2}$ terms together and noting the fact that the first term in the above integral becomes zero because $\langle \hat{x} \rangle = 0$ as shown above, we find that

$$\langle \hat{p} \rangle = \frac{\hbar}{i} N_v^2 \sqrt{\gamma} \int_{-\infty}^{\infty} e^{-\gamma x^2} H_v(\sqrt{\gamma} x) H_{v'}(\sqrt{\gamma} x)$$
$$= \frac{\hbar}{i} N_v^2 \int_{-\infty}^{\infty} d\xi e^{-\xi^2} H_v(\xi) H_v'(\xi)$$
$$= \frac{\hbar}{i} 2v N_v^2 \int_{-\infty}^{\infty} d\xi e^{-\xi^2} H_v(\xi) H_{v-1}(\xi) = 0,$$

where the identity involving the derivative of Hermite polynomial, Eq. (3.35) and the orthogonality of the eigenstates of the vibrational Hamiltonian were used.

3.5 For the lowest two eigenstates of a harmonic oscillator $|0\rangle$ and $|1\rangle$, for which $m\omega = \hbar$, calculate $\langle 0|\hat{x}|1\rangle$ by explicitly evaluating the integration involving the expressions for the corresponding wavefunctions.

Solution 3.5 Expressing $|0\rangle$ and $|1\rangle$ in the position space,

$$\langle 0|\hat{x}|1\rangle = \int_{-\infty}^{\infty} \psi_0(x) x \psi_1(x)$$
$$= N_0 N_1 \int_{-\infty}^{\infty} dx e^{-\gamma x^2/2} H_0(\sqrt{\gamma} x) x e^{-\gamma x^2/2} H_1(\sqrt{\gamma} x)$$

$$= N_0 N_1 \int_{-\infty}^{\infty} dx e^{-\gamma x^2} x \cdot (2\sqrt{\gamma} x)$$

$$= \sqrt{\frac{2\gamma^2}{\pi}} \int_{-\infty}^{\infty} dx e^{-\gamma x^2} x^2 = \frac{1}{\sqrt{2\gamma}} = \frac{1}{\sqrt{2}},$$

where the fact that $\gamma = m\omega/\hbar = 1$ has been used.

3.6 Find out expressions for the position and momentum operators as linear combinations of raising and lowering operators $\hat{b}^\dagger$ and $\hat{b}$.

Solution 3.6 Summing Eqs. (3.51) and (3.52), we find that

$$\hat{b} + \hat{b}^\dagger = \sqrt{\frac{2m\omega}{\hbar}} \hat{x}.$$

Therefore,

$$\hat{x} = \sqrt{\frac{h}{2m\omega}} \left(\hat{b} + \hat{b}^\dagger \right).$$

On the other hand, subtracting Eq. (3.52) from Eq. (3.51), we find that

$$\hat{b} - \hat{b}^\dagger = i \sqrt{\frac{2}{m\hbar\omega}} \hat{p}.$$

Therefore,

$$\hat{p} = \sqrt{\frac{m\hbar\omega}{2}} \frac{1}{i} \left(\hat{b} - \hat{b}^\dagger \right).$$

3.7 For a harmonic oscillator with mass m and angular frequency ω, find out the expression for $\hat{p}^2$, the square of the momentum operator, in terms of lowering and raising operators $\hat{b}$ and $\hat{b}^\dagger$. Use this expression to calculate $\langle 0|\hat{p}^2|0\rangle$, where $|0\rangle$ is the ground eigenstate of the harmonic oscillator Hamiltonian.

Solution 3.7 The momentum operator $\hat{p}$ can be expressed as

$$\hat{p} = \sqrt{\frac{m\hbar\omega}{2}} \frac{1}{i} \left(\hat{b} - \hat{b}^\dagger \right).$$

Taking square of the above expression, we obtain

$$\hat{p}^2 = -\frac{m\hbar\omega}{2} (\hat{b} - \hat{b}^\dagger)^2 = -\frac{m\hbar\omega}{2} \left(\hat{b}^2 - \hat{b}\hat{b}^\dagger - \hat{b}^\dagger \hat{b} + \hat{b}^{\dagger 2} \right).$$

Therefore,

$$\langle 0|\hat{p}^2|0\rangle = \frac{m\hbar\omega}{2}\langle 0|\left(-\hat{b}^2 + \hat{b}\hat{b}^\dagger + \hat{b}^\dagger\hat{b} - \hat{b}^{\dagger 2}\right)|0\rangle = \frac{m\hbar\omega}{2}\langle 0|\hat{b}\hat{b}^\dagger|0\rangle = \frac{m\hbar\omega}{2}.$$

3.8 Given that the state of a harmonic oscillator with unit mass and unit angular frequency, namely, $m = \omega = 1$, is in the following state at time t=0:

$$|\psi\rangle = \frac{1}{\sqrt{2}}\left(|0\rangle + |1\rangle\right),$$

find out expression for the time dependent expectation value of the position $\langle\hat{x}(t)\rangle = \langle\psi; t|\hat{x}|\psi; t\rangle$.

Solution 3.8 The state at time t is given by

$$|\psi; t\rangle = \frac{1}{\sqrt{2}}\left(e^{-i\omega t/2}|0\rangle + e^{-3i\omega t/2}|1\rangle\right).$$

Therefore,

$$\langle\hat{x}(t)\rangle = \frac{1}{2}\left(\langle 0|\hat{x}|0\rangle + e^{-i\omega t}\langle 0|\hat{x}|1\rangle + e^{i\omega t}\langle 1|\hat{x}|0\rangle + \langle 1|\hat{x}|1\rangle\right).$$

On the righthand side of the above expression,

$$\langle 0|\hat{x}|0\rangle = \langle 1|\hat{x}|1\rangle = 0.$$

On the other hand,

$$\langle 0|\hat{x}|1\rangle = \langle 1|\hat{x}|0\rangle = N_0 N_1 \frac{1}{\gamma}\frac{\sqrt{\gamma}}{N_0^2} = \frac{1}{\sqrt{\gamma}}\frac{N_0}{N_1} = \frac{1}{\sqrt{2\gamma}},$$

where Eq. (3.46) has been used. As a result,

$$\langle\hat{x}(t)\rangle = \frac{1}{\sqrt{2\gamma}}\cos(\omega t).$$

3.9 For any eigenstate $|v\rangle$ of a harmonic oscillator with angular frequency ω, prove the following identities:

$$\text{I}: e^{i\hat{H}t/\hbar}\hat{b}e^{-i\hat{H}t/\hbar}|v\rangle = e^{-i\omega t}\hat{b}|v\rangle,$$

$$\text{II}: e^{i\hat{H}t/\hbar}\hat{b}^\dagger e^{-i\hat{H}t/\hbar}|v\rangle = e^{i\omega t}\hat{b}^\dagger|v\rangle.$$

Solution 3.9 The identity I can be proved as follows. First, using

$$e^{-i\hat{H}t/\hbar}|v\rangle = e^{-i\omega(v+1/2)t}|v\rangle,$$

one can show that

$$e^{i\hat{H}t/\hbar}\hat{b}e^{-i\hat{H}t/\hbar}|v\rangle = \left(e^{i\hat{H}t/\hbar}\hat{b}|v\rangle\right)e^{-i\omega(v+1/2)t}.$$

Since $\hat{b}|v\rangle$ is an eigenstate of $\hat{H}$ with eigenvalue $\hbar\omega(v-1+1/2) = \hbar\omega(v-1/2)$,

$$e^{i\hat{H}t/\hbar}\hat{b}|v\rangle = e^{i\omega(v-1/2)t}\hat{b}|v\rangle.$$

Therefore,

$$\text{I}: e^{i\hat{H}t/\hbar}\hat{b}e^{-i\hat{H}t/\hbar}|v\rangle = e^{i\omega(v-1/2)t}e^{-i\omega(v+1/2)t}\hat{b}|v\rangle = e^{-i\omega t}\hat{b}|v\rangle.$$

Similarly, the identity II can be proved first recognizing that

$$e^{i\hat{H}t/\hbar}\hat{b}^\dagger e^{-i\hat{H}t/\hbar}|v\rangle = e^{i\hat{H}t/\hbar}\hat{b}^\dagger|v\rangle e^{-i\omega(v+1/2)t}.$$

Since $\hat{b}^\dagger|v\rangle$ is an eigenstate of $\hat{H}$ with eigenvalue $\hbar\omega(v+1/2) = \hbar\omega(v+3/2)$,

$$e^{i\hat{H}t/\hbar}\hat{b}^\dagger|v\rangle = e^{i\omega(v+3/2)t}\hat{b}^\dagger|v\rangle.$$

Therefore,

$$\text{II}: e^{i\hat{H}t/\hbar}\hat{b}^\dagger e^{-i\hat{H}t/\hbar}|v\rangle = e^{i\omega(v+3/2)t}e^{-i\omega(v+1/2)t}\hat{b}^\dagger|v\rangle = e^{i\omega t}\hat{b}^\dagger|v\rangle.$$

3.10 For the following diatomic molecules with fundamental vibrational frequencies (in wavenumber) as shown, calculate their respective force constants in the unit of dyne $\text{cm}^{-1} = \text{g s}^{-2}$. Assuming that there are no anharmonic effects, determine whether each of the molecules is IR and/or Raman active. Explain the reason for your answer and also determine the frequency of transition for each case.

(a) H_2 ($\tilde{\nu}_e = 2321\,\text{cm}^{-1}$)
(b) $^{16}O_2$ ($\tilde{\nu}_e = 1510\,\text{cm}^{-1}$)
(c) HCl ($\tilde{\nu}_e = 1529\,\text{cm}^{-1}$)
(d) DCl ($\tilde{\nu}_e = 1220\,\text{cm}^{-1}$)

Solution 3.10 Note that $\tilde{\nu}_e = \tilde{\omega}_e/(2\pi c) = \sqrt{k/\mu}/(2\pi c)$, where k and μ are spring constant and reduced mass. Thus, $k = (2\pi c\tilde{\nu}_e)^2\mu$. The table below shows these data for the four molecules.

Molecule	μ (a.m.u.)	μ (g)	$2\pi c\tilde{\nu}_e$ (s^{-1})	k (gs^{-2})
H_2	0.5	8.31×10^{-25}	4.38×10^{14}	1.59×10^5
$^{16}O_2$	8	1.33×10^{-23}	2.84×10^{14}	1.07×10^6
HCl	0.97	1.61×10^{-24}	2.88×10^{14}	1.34×10^5
DCl	1.89	3.14×10^{-24}	2.30×10^{14}	1.66×10^5

Note that H_2 and $^{16}O_2$ are only Raman active because they are symmetric while HCl and DCl are both IR and Raman active.

3.11 For a certain heteroatomic diatomic molecule, its vibrational term can be approximated well by the following expression:

$$G_v = \tilde{\nu}_e \left(v + \frac{1}{2}\right) - 0.1\tilde{\nu}_e \left(v + \frac{1}{2}\right)^2.$$

It is known that the molecule is either in the ground vibrational state $v = 0$ or the first excited vibrational state $v = 1$. Assuming that the same selection rules for harmonic oscillator apply, find out expressions for all possible frequencies of IR absorption, Raman Stokes, and Raman Anti-Stokes frequencies.

Solution 3.11 The IR absorption and Raman stokes transitions are the same and correspond to v: $0 \rightarrow 1$ or $1 \rightarrow 2$.

The wavenumber of the photon absorbed in IR or the red shift in Stokes Raman can be calculated as follows.
For v: $0 \rightarrow 1$,

$$\begin{aligned} G_1 - G_0 &= \tilde{\nu}_e \frac{3}{2} - 0.1\tilde{\nu}_e \frac{9}{4} - \left(\tilde{\nu}_e \frac{1}{2} - 0.1\tilde{\nu}_e \frac{1}{4}\right) \\ &= \tilde{\nu}_e \left(\frac{3}{2} - \frac{9}{40} - \frac{1}{2} + \frac{1}{40}\right) = 0.8\tilde{\nu}_e. \end{aligned}$$

For v: $1 \rightarrow 2$,

$$\begin{aligned} G_2 - G_1 &= \tilde{\nu}_e \frac{5}{2} - 0.1\tilde{\nu}_e \frac{25}{4} - \left(\tilde{\nu}_e \frac{3}{2} - 0.1\tilde{\nu}_e \frac{9}{4}\right) \\ &= \tilde{\nu}_e \left(\frac{5}{2} - \frac{25}{40} - \frac{3}{2} + \frac{9}{40}\right) = 0.6\tilde{\nu}_e. \end{aligned}$$

There is only one Raman Anti-Stokes, v: $1 \rightarrow 0$, for which $G_1 - G_0 = 0.8\tilde{\nu}$ as shown above.

Problems

3.12 A quantum harmonic oscillator with unit mass and angular frequency, *i.e.*, $m = \omega = 1$, is in the first excited eigenstate of the Hamiltonian, $|1\rangle$, for which the eigenvalue is equal to $3\hbar/2$. Determine the uncertainties in position and momentum, σ_x and σ_p, and show that they satisfy the uncertainty relationship.

3.13 Use the recursion relationship Eq. (3.34) and answers in **Solution 3.3** to find out expressions for $H_6(\xi)$ and $H_7(\xi)$.

3.14 For a quantum harmonic oscillator with mass m and angular frequency ω, find out expression for $\hat{x}^2$ in terms of the lowering and raising operators, $\hat{b}$ and $\hat{b}^\dagger$. Then, use this expression to calculate $\langle 2|\hat{x}^2|2\rangle$, where $|2\rangle$ is the eigenstate of the Hamiltonian with eigenvalue $E_2 = 5\hbar\omega/2$.

3.15 Given that the state of a harmonic oscillator with unit mass and angular frequency, namely, $m = \omega = 1$, is in the following state at time $t = 0$:

$$|\psi; 0\rangle = \frac{1}{\sqrt{2}} \left(|0\rangle + i|1\rangle\right),$$

where $|0\rangle$ and $|1\rangle$ are the ground and first excited states of the Hamiltonian, calculate the expectation value of the energy for $|\psi; t = \pi\rangle$.

3.16 A quantum harmonic oscillator with unit mass ($m = 1$) and unit angular frequency ($\omega = 1$) at time $t = 0$ is in the linear superposition of its three normalized eigenstates of the Hamiltonian as follows:

$$|\psi; 0\rangle = \frac{1}{\sqrt{3}}|0\rangle - \frac{i}{\sqrt{3}}|1\rangle + \frac{1}{\sqrt{3}}|3\rangle,$$

where the eigenvalue for $|v\rangle$ is $\hbar(v + 1/2)$. Calculate the expectation value of the position for $|\psi; t = \pi\rangle$.

3.17 The vibrational term for HBr, where the atomic numbers of H and Br are respectively 1 and 79, is given by

$$G_v = \tilde{\nu}_e \left(v + \frac{1}{2}\right) - x_e\tilde{\nu}_e \left(v + \frac{1}{2}\right)^2,$$

with $\nu_e = 2649.67\ \text{cm}^{-1}$ and $x_e\tilde{\nu}_e = 45.21\ \text{cm}^{-1}$. It is known that the molecule is in one of the three vibrational states with $v = 0$, 1, and 2. Assuming that the same selection rules for harmonic oscillator apply, find out expressions for all possible frequencies of IR absorption, Raman Stokes, and Raman anti-Stokes frequencies.

3.18 For a certain homonuclear diatomic molecule, its vibrational term can be approximated well by the following expression:

$$G_v = \tilde{\nu}_e \left(v + \frac{1}{2} \right) - 0.1 \tilde{\nu}_e \left(v + \frac{1}{2} \right)^2.$$

It is known that the molecule is in one of the two states with $v = 0$ and 1. Assuming that the same selection rules for harmonic oscillator apply, find out expressions for all possible Raman Stokes frequencies in the unit of $\tilde{\nu}_e$.

Chapter 4
Multidimensional Systems and Separation of Variables



There's no sense in being precise when you don't even know what you're talking about.

— John von Neumann

Abstract This chapter provides time independent Schrödinger equations for a quantum particle in three dimensional space and many interacting quantum particles in multidimensional space. As the simplest example, a quantum particle in a three dimensional box is considered. The corresponding eigenvalues and eigenfunctions are provided employing the separation of variables method. These solutions are used to illustrate the concept of degeneracy. Then, a more general description of the separation of variables method is provided. As an application, quantum mechanical description of the multidimensional vibrational motion of a polyatomic molecules, within the harmonic oscillator approximation for each normal mode, is presented.

So far, we have considered one dimensional motion in order to understand the principles and features of quantum mechanics as clearly as possible. However, hardly anything is one dimensional. Typically, the motion of a single particle needs to be considered in three dimensional physical space. If there are N particles interacting in three dimensional space, we need to consider a $3N$ dimensional mathematical space in order to provide complete description of the system even for the description within the classical mechanics.

It turns out that extending quantum mechanical position and momentum operators and their corresponding eigenstates to multidimensional spaces is straightforward at least in Cartesian coordinate systems, where one dimensional position and momentum states along each direction can be combined independently to form the multidimensional space. The corresponding states can also be defined in a

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straightforward manner by direct products, as defined in Sect. 2.5. This results in expansion of the dimension of the corresponding vector space of states to that of the power of $3N$. This chapter provides detailed consideration of these states and introduces a simple separation of variables method for solving the multidimensional Schrödinger equation.

4.1 Three Dimensional System

4.1.1 Position, Momentum, Hamiltonian, and Schrödinger Equation

The position and momentum operator defined in one dimension can be extended to three dimension through a direct product of those for x, y, and z as described in Sect. 2.5. This then allows straightforward extension of Schrödinger's equation to three dimension.

Taking the Hermitian adjoint of the three dimensional position ket $|\mathbf{r}\rangle$ defined by Eq. (2.93), leads to the following three dimensional position bra:

$$\langle\mathbf{r}| = \langle x| \otimes \langle y| \otimes \langle z|. \tag{4.1}$$

Then, for a quantum mechanical state $|\psi\rangle$ representing a particle in three dimension, the value of the corresponding Schrödinger's wave function at $\mathbf{r}$ can be defined as the following inner product:

$$\psi(\mathbf{r}) = \langle\mathbf{r}|\psi\rangle. \tag{4.2}$$

If $|\psi\rangle$ corresponds to another position ket $|\mathbf{r}'\rangle$, the above identity leads to the three dimensional Dirac-delta function as follows:[1]

$$\delta(\mathbf{r}-\mathbf{r}') = \langle\mathbf{r}|\mathbf{r}'\rangle. \tag{4.3}$$

The above identities are equivalent to the following completeness relation that expresses the identity operator in terms of outer products of positions states.

[1] This three dimensional Dirac delta function, or distribution, satisfies the two conditions that $\int d\mathbf{r}'\delta(\mathbf{r}-\mathbf{r}')f(\mathbf{r}') = f(\mathbf{r})$ for any integrable function $f(\mathbf{r})$ and $\delta(\mathbf{r}-\mathbf{r}') = 0$ for $\mathbf{r} \neq \mathbf{r}'$, where $\int d\mathbf{r} = \int dx \int dy \int dz$ in the Cartesian coordinate system.

Completeness of Three Dimensional States

Three dimensional position states form a complete basis and integration of its outer products over the entire space is equal to the identity operator as expressed below.

$$\hat{1} = \int d\mathbf{r}|\mathbf{r}\rangle\langle\mathbf{r}| = \lim_{\delta\mathbf{r}\to 0}\sum_i \delta\mathbf{r}|\mathbf{r}_i\rangle\langle\mathbf{r}_i|. \tag{4.4}$$

The above identity is a three dimensional analogue of Eq. (2.25) and the second equality simply represents the mathematical definition of the integration as the limit of the sum over smaller volume elements $\delta\mathbf{r}$ becoming infinitesimally small.

The above completeness relation implies that any quantum mechanical state $|\psi\rangle$ describing a quantum particle in three dimensional space can be represented as a linear combination of the position states. Thus,

$$|\psi\rangle = \int d\mathbf{r}\ |\mathbf{r}\rangle\langle\mathbf{r}|\psi\rangle = \int d\mathbf{r}\ \psi(\mathbf{r})|\mathbf{r}\rangle = \lim_{\delta\mathbf{r}\to 0}\sum_i \delta\mathbf{r}\psi(\mathbf{r}_i)|\mathbf{r}_i\rangle, \tag{4.5}$$

where Eq. (4.2) has been used. The second equality in the above equation shows that $\delta\mathbf{r}\psi(\mathbf{r}_i)$ is nothing but the coefficient for $|\mathbf{r}_i\rangle$ in the representation of the state as a linear combination of the position states.

Taking the Hermitian adjoint of Eq. (2.94), we obtain

$$\langle\mathbf{r}|\hat{\mathbf{r}} = \langle\mathbf{r}|\mathbf{r} = \mathbf{r}\langle\mathbf{r}|, \tag{4.6}$$

where the fact that the position operator is a Hermitian operator and that $\mathbf{r}$ is a real-valued vector has been used. Applying the above identity to a state ket $|\psi\rangle$, we then obtain

$$\langle\mathbf{r}|\hat{\mathbf{r}}|\psi\rangle = \mathbf{r}\langle\mathbf{r}|\psi\rangle = \mathbf{r}\psi(\mathbf{r}), \tag{4.7}$$

which is a three dimensional generalization of Eq. (2.24). Application of this identity for the case where the state is $\hat{\mathbf{r}}|\psi\rangle$ leads to

$$\begin{aligned}\langle\mathbf{r}||\hat{\mathbf{r}}|^2|\psi\rangle &= \langle\mathbf{r}|\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}|\psi\rangle \\ &= \langle\mathbf{r}|\hat{\mathbf{r}}\cdot\big(\hat{\mathbf{r}}|\psi\rangle\big) \\ &= \mathbf{r}\cdot\langle\mathbf{r}|\hat{\mathbf{r}}|\psi\rangle \\ &= \mathbf{r}\cdot\mathbf{r}\langle\mathbf{r}|\psi\rangle = |\mathbf{r}|^2\langle\mathbf{r}|\psi\rangle.\end{aligned} \tag{4.8}$$

For any function $V(\mathbf{r})$, one can use Eq. (4.7) repeatedly for a Taylor expansion of $V(\mathbf{r})$ and obtain

$$\langle \mathbf{r}|V(\hat{\mathbf{r}})|\psi\rangle = V(\mathbf{r})\langle \mathbf{r}|\psi\rangle = V(\mathbf{r})\psi(\mathbf{r}). \tag{4.9}$$

In other words, applying an operator $V(\hat{\mathbf{r}})$ to a state $|\psi\rangle$ simply amounts to multiplying $\psi(\mathbf{r})$ (the position representation of $|\psi\rangle$) with the function $V(\mathbf{r})$.

As the next step, let us consider the momentum operator in the three dimensional space, $\hat{\mathbf{p}} = \hat{p}_x\mathbf{e}_x + \hat{p}_y\mathbf{e}_y + \hat{p}_z\mathbf{e}_z$, as introduced in Sect. 2.5. Here, each component is defined by its effect on the corresponding position ket as follows:

$$\hat{p}_x|x\rangle = -\frac{\hbar}{i}\frac{\partial}{\partial x}|x\rangle, \tag{4.10}$$

$$\hat{p}_y|y\rangle = -\frac{\hbar}{i}\frac{\partial}{\partial y}|y\rangle, \tag{4.11}$$

$$\hat{p}_z|z\rangle = -\frac{\hbar}{i}\frac{\partial}{\partial z}|z\rangle. \tag{4.12}$$

On the other, each component does not have any effect on the position states of other components. For example, $\hat{p}_x$ does not have any effect on $|y\rangle$ and $|z\rangle$. Therefore, application of $\hat{\mathbf{p}}$ to $|\mathbf{r}\rangle$ leads to

$$\begin{aligned}\hat{\mathbf{p}}|\mathbf{r}\rangle &= (\hat{p}_x\mathbf{e}_x + \hat{p}_y\mathbf{e}_y + \hat{p}_z\mathbf{e}_z)|x\rangle \otimes |y\rangle \otimes |z\rangle \\ &= \mathbf{e}_x\left(\hat{p}_x|x\rangle\right) \otimes |y\rangle \otimes |z\rangle + \mathbf{e}_y|x\rangle \otimes \left(\hat{p}_y|y\rangle\right) \otimes |z\rangle + \mathbf{e}_z|x\rangle \otimes |y\rangle \otimes (p_z|z\rangle) \\ &= -\frac{\hbar}{i}\boldsymbol{\nabla}|\mathbf{r}\rangle,\end{aligned} \tag{4.13}$$

where

$$\nabla = \mathbf{e}_x\frac{\partial}{\partial x} + \mathbf{e}_y\frac{\partial}{\partial y} + \mathbf{e}_z\frac{\partial}{\partial z}. \tag{4.14}$$

The Hermitian adjoint of Eq. (4.13) is

$$\langle \mathbf{r}|\hat{\mathbf{p}} = \frac{\hbar}{i}\boldsymbol{\nabla}\langle \mathbf{r}|. \tag{4.15}$$

Taking inner product of the above identity with an arbitrary ket $|\psi\rangle$, we find a key identity that establishes the effect of momentum operation on arbitrary state as described below.

Implication of Three Dimensional Momentum Operation

For an arbitrary state $|\psi\rangle$,

$$\langle \mathbf{r}|\hat{\mathbf{p}}|\psi\rangle = \frac{\hbar}{i}\nabla\langle \mathbf{r}|\psi\rangle = \frac{\hbar}{i}\nabla\psi(\mathbf{r}). \quad (4.16)$$

The last term in the above equation is the definition of the momentum operator in Schrödinger's formulation of quantum mechanics. The complex conjugate of the above identity is

$$\langle \psi|\hat{\mathbf{p}}|\mathbf{r}\rangle = \big(\langle \mathbf{r}|\hat{\mathbf{p}}|\psi\rangle\big)^* = -\frac{\hbar}{i}\nabla\psi^*(\mathbf{r}) = -\frac{\hbar}{i}\nabla\langle\psi|\mathbf{r}\rangle. \quad (4.17)$$

This identity can in fact be obtained more easily by taking the inner product of Eq. (4.13) with $\langle\psi|$ and employing the fact that $\langle\psi|\nabla|\mathbf{r}\rangle = \nabla\langle\psi|\mathbf{r}\rangle$.

In a way similar to Eq. (4.8), application of Eq. (4.16) twice leads to

$$\langle \mathbf{r}||\hat{\mathbf{p}}|^2|\psi\rangle = \langle \mathbf{r}|\hat{\mathbf{p}}\cdot\hat{\mathbf{p}}|\psi\rangle = \frac{\hbar}{i}\nabla\cdot\langle \mathbf{r}|\hat{\mathbf{p}}|\psi\rangle = -\hbar^2\nabla^2\langle \mathbf{r}|\psi\rangle = -\hbar^2\nabla^2\psi(\mathbf{r}), \quad (4.18)$$

where note that $|\hat{\mathbf{p}}|^2 = \hat{\mathbf{p}}\cdot\hat{\mathbf{p}} = \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2$ and

$$\nabla^2 = \nabla\cdot\nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \quad (4.19)$$

Summing up all the definitions and identities provided above, now we can find a general expression for the time independent Schrödinger equation for a particle in three dimensional space as describe below.

Time Independent Schrödinger Equation in Three Dimension

The Hamiltonian operator for a quantum mechanical particle subject to a potential energy $V(\mathbf{r})$ in a three dimensional space is

$$\hat{H} = \frac{|\hat{\mathbf{p}}|^2}{2m} + V(\hat{\mathbf{r}}). \quad (4.20)$$

(continued)

Thus, the time independent Schrödinger equation for the particle in the Dirac notation is

$$\hat{H}|\psi_E\rangle \equiv \left(\frac{|\hat{\mathbf{p}}|^2}{2m} + V(\hat{\mathbf{r}})\right)|\psi_E\rangle = E|\psi_E\rangle, \tag{4.21}$$

where $|\psi_E\rangle$ is the eigenket of $\hat{H}$ with energy E. Taking inner product of the above equation with $\langle\mathbf{r}|$ and using Eqs. (4.9) and (4.18), one can obtain the original Schrödinger's equation for time independent wavefunction in three-dimensional space,

$$\langle\mathbf{r}|\hat{H}|\psi_E\rangle \equiv \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi_E(\mathbf{r}) = E\psi_E(\mathbf{r}), \tag{4.22}$$

where $\psi_E(\mathbf{r}) \equiv \langle\mathbf{r}|\psi_E\rangle$. The above equation is the position representation of the Schrödinger equation in the Dirac notation. Solving this time independent Schrödinger equation is an important first step for understanding the behavior of a given quantum particle in a three dimensional space. While finding an exact closed form solution of the above equation for a general three dimensional potential is difficult, a simple method of solution exists for the case where the potential energy can be separated into one dimensional terms.

4.1.2 *Particle in a Three Dimensional Rectangular Box*

As the simplest example, let us consider a quantum particle in the following three dimensional rectangular box (see Fig. 4.1):

$$V_{3D-box}(\mathbf{r}) = \begin{cases} 0\,, & 0 < x < a,\ 0 < y < b,\ 0 < z < c \ \leftarrow \text{ Region I} \\ \infty\,, & \text{otherwise} \qquad\qquad\qquad \leftarrow \text{ Region II} \end{cases} \tag{4.23}$$

For this potential, it is easy to find $\psi_E(\mathbf{r}) = \langle\mathbf{r}|\psi_E\rangle$ and eigenvalue E satisfying the Schrödinger equation, Eq. (4.22).

For now, let us denote the wavefunction satisfying the time independent Schrödinger equation for energy E as $\psi(\mathbf{r})$. First, for the region II in Eq. (4.23), it is clear that $\psi(\mathbf{r}) = 0$. Otherwise, the energy becomes infinity, which is not an acceptable solution. This imposes the following boundary condition to be satisfied by the finite wave function in region I:

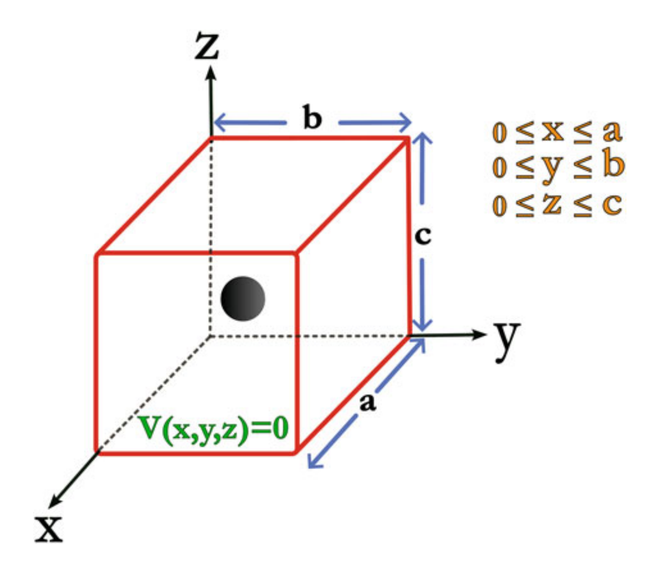


Fig. 4.1 Three dimensional box with sides a, b, and c along x, y, and z directions

$$\psi(0, y, z) = \psi(a, y, z) = \psi(x, 0, z) = \psi(x, b, z)$$
$$= \psi(x, y, 0) = \psi(x, y, c) = 0. \tag{4.24}$$

Along with the above boundary condition, Eq. (4.22) for region I reduces to

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{4.25}$$

This equation can be solved by making the following assumptions:

$$\psi(\mathbf{r}) = X(x)Y(y)Z(z), \tag{4.26}$$
$$E = E_x + E_y + E_z. \tag{4.27}$$

Inserting Eqs. (4.26) and (4.27) into Eq. (4.25), moving $E\psi(\mathbf{r})$ to the lefthand side, and dividing the whole equation with $-\hbar^2/(2m)$, we find that

$$\left(\frac{d^2X(x)}{dx^2} + \frac{2mE_x}{\hbar^2}X(x)\right)Y(y)Z(z)$$
$$+\left(\frac{d^2Y(y)}{dy^2} + \frac{2mE_y}{\hbar^2}Y(y)\right)X(x)Z(z)$$
$$+\left(\frac{d^2Z(z)}{dz^2} + \frac{2mE_z}{\hbar^2}Z(z)\right)X(x)Y(y) = 0. \tag{4.28}$$

Let us divide the above equation with $X(x)Y(y)Z(z)$ (assuming that this is nonzero). Then, it becomes

$$
\begin{aligned}
&\frac{1}{X(x)}\left(\frac{d^2X(x)}{dx^2}+\frac{2mE_x}{\hbar^2}X(x)\right)\\
&+\frac{1}{Y(y)}\left(\frac{d^2Y(y)}{dy^2}+\frac{2mE_y}{\hbar^2}Y(y)\right)\\
&+\frac{1}{Z(z)}\left(\frac{d^2Z(z)}{dz^2}+\frac{2mE_z}{\hbar^2}Z(z)\right)=0.
\end{aligned}
\tag{4.29}
$$

The above equation shows that the sum of three independent functions of x, y, and z, respectively, becomes zero. For this to be true in general, each term should become zero. Thus, the above equation, along with the boundary condition, Eq. (4.24), implies that

$$
\frac{d^2X(x)}{dx^2}+\frac{2mE_x}{\hbar^2}X(x)=0,\ \text{with } X(0)=X(a)=0, \tag{4.30}
$$

$$
\frac{d^2Y(y)}{dy^2}+\frac{2mE_y}{\hbar^2}Y(y)=0,\ \text{with } Y(0)=Y(b)=0, \tag{4.31}
$$

$$
\frac{d^2Z(z)}{dz^2}+\frac{2mE_z}{\hbar^2}Z(z)=0,\ \text{with } Z(0)=Z(c)=0. \tag{4.32}
$$

Note that each of the above equation corresponds to that for the one dimensional particle in a box problem that was considered in Sect. 1.4. Thus, the solutions for the above three equations are

$$
X_{n_x}(x)=\sqrt{\frac{2}{a}}\sin\left(\frac{n_x\pi x}{a}\right),\ E_{n_x}=\frac{\hbar^2n_x^2\pi^2}{2ma^2},\ n_x=1,2,\ldots \tag{4.33}
$$

$$
Y_{n_y}(y)=\sqrt{\frac{2}{b}}\sin\left(\frac{n_y\pi y}{a}\right),\ E_{n_y}=\frac{\hbar^2n_y^2\pi^2}{2mb^2},\ n_y=1,2,\ldots \tag{4.34}
$$

$$
Z_{n_z}(z)=\sqrt{\frac{2}{c}}\sin\left(\frac{n_z\pi z}{a}\right),\ E_{n_z}=\frac{\hbar^2n_z^2\pi^2}{2mc^2},\ n_z=1,2,\ldots \tag{4.35}
$$

Inserting these solutions into Eq. (4.26), we obtain the following eigenfunction

$$
\psi_{n_xn_yn_z}(\mathbf{r})=\sqrt{\frac{8}{abc}}\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{b}\right)\sin\left(\frac{n_z\pi z}{c}\right), \tag{4.36}
$$

with the eigenvalue

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right). \tag{4.37}$$

In the Dirac notation, the eigenstates can simply be represented by $|n_x, n_y, n_z\rangle = |n_x\rangle \otimes |n_y\rangle \otimes |n_z\rangle$. The kets comprising this direct product are related to the wavefunctions given above as follows: $X_{n_x}(x) = \langle x|n_x\rangle$; $Y_{n_y}(y) = \langle y|n_y\rangle$; $Z_{n_z}(z) = \langle z|n_z\rangle$. Thus, $|n_x, n_y, n_z\rangle$ satisfies the following time independent Schrödinger equation (in the Dirac notation):

$$\hat{H}|n_x, n_y, n_z\rangle = \left(\frac{|\hat{\mathbf{p}}|^2}{2m} + \hat{V}_{3D-box} \right) |n_x, n_y, n_z\rangle = E_{n_x n_y n_z} |n_x, n_y, n_z\rangle. \tag{4.38}$$

In the above expression, $\hat{V}_{3D-box}$ corresponding to Eq. (4.23) is defined as

$$\hat{V}_{3D-box}|\mathbf{r}\rangle = V_{3D-box}(\mathbf{r})|\mathbf{r}\rangle. \tag{4.39}$$

Although the eigenstates defined by Eq. (4.38) have been determined under the assumption that the state is a product of those for each Cartesian coordinates, the general quantum states need not necessarily be such product states. This is because the state of a quantum particle in a box can be represented by the following linear combination of eigenstates:

$$|\psi\rangle = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} C_{n_x,n_y,n_z} |n_x, n_y, n_z\rangle. \tag{4.40}$$

Then, the corresponding wavefunction $\psi(\mathbf{r}) = \langle \mathbf{r}|\psi\rangle$ is expressed as

$$\psi(\mathbf{r}) = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} C_{n_x,n_y,n_z} \psi_{n_x n_y n_z}(\mathbf{r}). \tag{4.41}$$

It is well-known mathematically that the above expression can represent any well-behaving function of **r**. Thus, the solutions based on the assumption of separation of variables can be used to represent any well-behaving non-separable wavefunctions as long as the same boundary conditions are satisfied.

If Eq. (4.40) is the state at time $t = 0$, then the state at time t becomes

$$|\psi; t\rangle = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} C_{n_x,n_y,n_z} e^{-i(E_{n_x}+E_{n_y}+E_{n_Z})t/\hbar} |n_x, n_y, n_z\rangle. \tag{4.42}$$

The corresponding time dependent wavefunction $\psi(\mathbf{r}; t) = \langle \mathbf{r}|\psi; t\rangle$ is expressed as

$$\psi(\mathbf{r}; t) = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} C_{n_x,n_y,n_z} e^{-i(E_{n_x}+E_{n_y}+E_{n_Z})t/\hbar}\psi_{n_x n_y n_z}(\mathbf{r}). \tag{4.43}$$

Having described a simple three dimensional system, it is now appropriate to explain the concept of degeneracy, which plays an important role in quantum mechanics. For a general case where $a \neq b \neq c$ and none of them is an integer multiple of the other, the energy eigenvalue $E_{n_x n_y n_z}$ is different for each set of (n_x, n_y, n_z). However, in case the box becomes more symmetrical, some of the energies become the same, namely, "degenerate." In that case, that particular energy is said to have *degeneracy* and the corresponding quantum states are called *degenerate*.

As an example, let us consider the case where $a = b = c$. In this case, Eq. (4.37) reduces to

$$E_{n_x n_y n_z} = \frac{\hbar^2\pi^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right), \tag{4.44}$$

where $n_x, n_y, n_z = 1, 2, 3, \ldots$. While the ground state $|1, 1, 1\rangle$ with energy E_{111} is non-degenerate, the first excited states $|2, 1, 1\rangle$, $|1, 2, 1\rangle$, and $|1, 1, 2\rangle$ are degenerate with a common eigenvalue E_{211}. Thus, the degeneracy of this eigenvalue is 3. It is important to note that any linear combination of degenerate eigenstates remains the eigenstate. This is obvious because application of the Hamiltonian to such a state results in the same eigenvalue that can be factored out. For example, any linear combination of $|2, 1, 1\rangle$, $|1, 2, 1\rangle$, and $|1, 1, 2\rangle$ is an eigenstate of $\hat{H}$ with eigenvalue E_{211}.

4.1.3 Separation in Cartesian Coordinate System

The three dimensional particle in a box problem is a special case of a more general situation where the three dimensional Schrödinger equation can be separated into three one dimensional equations. As long as the potential is given by a sum of three terms as

$$V(\mathbf{r}) = V_x(x) + V_y(y) + V_z(z), \tag{4.45}$$

and the boundary condition in each direction is independent of the other coordinates, one can assume that the energy is given by the sum of three terms as

$$E = E_x + E_y + E_z, \tag{4.46}$$

and the eigenfunction of the Hamiltonian can be assumed to have the following factorized form:

$$\psi(\mathbf{r}) = \psi_x(x)\psi_y(y)\psi_z(z). \tag{4.47}$$

Then, employing the separation of variables method as was done for the case of the particle in a three dimensional box, it is straightforward to show that the Schrödinger equation for the particle can be satisfied through the following three one dimensional equations:

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V_x(x)\right)\psi_x(x) = E_x\psi_x(x), \tag{4.48}$$

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dy^2} + V_y(y)\right)\psi_y(y) = E_y\psi_y(y), \tag{4.49}$$

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dz^2} + V_z(z)\right)\psi_z(z) = E_z\psi_z(z). \tag{4.50}$$

As an example, consider a three dimensional harmonic oscillator, for which the potential energy is given by

$$V(\mathbf{r}) = \frac{m}{2}(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2). \tag{4.51}$$

This potential is a sum of three independent terms along the three directions. Solving one dimensional harmonic oscillator problem in each direction and combining the solution, one finds that

$$E_{n_x,n_y,n_z} = \hbar\left[\omega_x\left(n_x + \frac{1}{2}\right) + \omega_y\left(n_y + \frac{1}{2}\right) + \omega_z\left(n_z + \frac{1}{2}\right)\right], \tag{4.52}$$

where $n_x, n_y, n_z = 0, 1, 2, \ldots$ and

$$\psi_{n_x n_y n_z}(\mathbf{r}) = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z), \tag{4.53}$$

with

$$\psi_{n_x}(x) = \frac{1}{\sqrt{2^{n_x} n_x!}}\left(\frac{\gamma_x}{\pi}\right)^{1/4} e^{-\gamma_x x^2/2} H_{n_x}(\sqrt{\gamma_x}x), \tag{4.54}$$

$$\psi_{n_y}(y) = \frac{1}{\sqrt{2^{n_y} n_y!}}\left(\frac{\gamma_y}{\pi}\right)^{1/4} e^{-\gamma_y y^2/2} H_{n_y}(\sqrt{\gamma_y}y), \tag{4.55}$$

$$\psi_{n_z}(z) = \frac{1}{\sqrt{2^{n_z} n_z!}}\left(\frac{\gamma_z}{\pi}\right)^{1/4} e^{-\gamma_z z^2/2} H_{n_z}(\sqrt{\gamma_z}z), \tag{4.56}$$

where $\gamma_p = m\omega_p/\hbar$ with $p = x, y$, and z, and H_n represents the nth order Hermite polynomial.

In the Dirac notation, the eigenstate of the three dimensional Harmonic oscillator can be expressed as

$$|n_x, n_y, n_z\rangle = |n_x\rangle|n_y\rangle|n_z\rangle \equiv |n_x\rangle \otimes |n_y\rangle \otimes |n_z\rangle. \tag{4.57}$$

The corresponding wavefunction in the position representation is obtained by taking the inner product of this state with a position state, $\langle \mathbf{r}| = \langle x|\langle y|\langle z| \equiv \langle x|\otimes\langle y|\otimes\langle z|$, as follows:

$$\begin{aligned} \psi_{n_x n_y n_z}(\mathbf{r}) &= \langle \mathbf{r}|n_x, n_y, n_z\rangle \\ &= \langle x|n_x\rangle\langle y|n_y\rangle\langle z|n_z\rangle = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z). \end{aligned} \tag{4.58}$$

4.2 Many Particle Systems and the Center of Mass Coordinates

The Hamiltonian operator for a quantum system consisting of N particles can be found by replacing their classical momentum and position with corresponding operators as follows:

$$\hat{H} = \frac{|\hat{\mathbf{p}}_1|^2}{2m_1} + \cdots + \frac{|\hat{\mathbf{p}}_N|^2}{2m_N} + V(\hat{\mathbf{r}}_1, \cdots, \hat{\mathbf{r}}_N), \tag{4.59}$$

where $\hat{\mathbf{p}}_k$ and $\hat{\mathbf{r}}_k$ for each of $k = 1, \cdots, N$ are momentum and position operators of particle k with mass m_k. For this many-particle system, one can construct $3N$ dimensional cartesian coordinates $\mathbf{R} = (\mathbf{r}_1, \cdots, \mathbf{r}_N)$, for which a position ket $|\mathbf{R}\rangle$ can be defined through direct products,

$$|\mathbf{R}\rangle = |\mathbf{r}_1\rangle \otimes \cdots \otimes |\mathbf{r}_N\rangle. \tag{4.60}$$

Let us denote a quantum state representing this N-particle system in the Dirac notation as $|\Psi_N\rangle$. Then, the corresponding wavefunction in the position representation is obtained by taking the inner product of this state with the multidimensional position bra as follows:

$$\Psi_N(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \langle \mathbf{R}|\Psi_N\rangle = \left(\langle \mathbf{r}_1| \otimes \cdots \otimes \langle \mathbf{r}_N|\right)|\Psi_N\rangle. \tag{4.61}$$

Note that $|\Psi_N\rangle$, even if it were an eigenstate, in general cannot be expressed as a direct product of the single particle states (unlike the position state) if the potential is not separable. Thus, the right hand side of the above expression cannot be simplified further unless there is some symmetry in the system.

One case of simplification that is fairly common is when the potential energy can be separated into those for the center of mass coordinates and remaining relative coordinates. Before considering this case in more detail, let us define the following center of mass coordinates,

$$\mathbf{r}_{cm} = \frac{m_1\mathbf{r}_1 + \cdots + m_N\mathbf{r}_N}{m_1 + \cdots + m_N}. \tag{4.62}$$

Then, let us also define new relative coordinates $\mathbf{r}'_1, \cdots, \mathbf{r}'_{N-1}$ that are orthogonal to each other and are independent of $\mathbf{r}_{cm}$. Then, the position ket for the total coordinates, Eq. (4.60), can alternatively be written as

$$|\mathbf{R}\rangle = |\mathbf{r}_{cm}\rangle \otimes |\mathbf{r}'_1\rangle \otimes \cdots \otimes |\mathbf{r}'_{N-1}\rangle. \tag{4.63}$$

Now assuming that the potential energy is separable as follows:

$$V(\hat{\mathbf{r}}_1, \cdots, \hat{\mathbf{r}}_N) = V_{cm}(\hat{\mathbf{r}}_{cm}) + V_{rel}(\hat{\mathbf{r}}'_1, \cdots, \hat{\mathbf{r}}'_{N-1}), \tag{4.64}$$

the Hamiltonian operator for the N particle system, Eq. (4.60), can be expressed as

$$\hat{H} = \frac{|\hat{\mathbf{p}}_{cm}|^2}{2M} + \frac{|\hat{\mathbf{p}}'_1|^2}{2m'_1} + \cdots + \frac{|\hat{\mathbf{p}}'_{N-1}|^2}{2m'_{N-1}} + V_{cm}(\hat{\mathbf{r}}_{cm}) + V_{rel}(\hat{\mathbf{r}}'_1, \cdots, \hat{\mathbf{r}}'_{N-1}), \tag{4.65}$$

where $\hat{\mathbf{p}}_{cm}$ and $\hat{\mathbf{p}}'_k$ (for $k = 1, \cdots, N-1$) are canonical momentum operators conjugate to $\hat{\mathbf{r}}_{cm}$ and $\hat{\mathbf{r}}'_k$, M is the total mass of the system and m'_k (for $k = 1, \cdots, N-1$) is the effective mass for the kth coordinate $\mathbf{r}'_k$. For the above Hamiltonian, an eigenstate can be assumed to be a product form as follows:

$$|\Psi_N\rangle = |\psi_{cm}\rangle \otimes |\psi_{rel}\rangle, \tag{4.66}$$

where $|\psi_{cm}\rangle$ and $|\psi_{rel}\rangle$ are eigenstates respectively satisfying the following Schrödinger equations:

$$\left(\frac{|\hat{\mathbf{p}}_{cm}|^2}{2M} + V_{cm}(\hat{\mathbf{r}}_{cm})\right)|\psi_{cm}\rangle = E_{cm}|\psi_{cm}\rangle, \tag{4.67}$$

$$\left(\frac{|\hat{\mathbf{p}}'_1|^2}{2m'_1} + \cdots + \frac{|\hat{\mathbf{p}}'_{N-1}|^2}{2m'_{N-1}} + V_{rel}(\hat{\mathbf{r}}'_1, \cdots, \hat{\mathbf{r}}'_{N-1})\right)|\psi_{rel}\rangle = E_{rel}|\psi_{rel}\rangle. \tag{4.68}$$

Then, the total wave function, the position representation of the state, can be expressed as

$$\begin{aligned}\Psi_N(\mathbf{R}) = \langle\mathbf{R}|\Psi_N\rangle &= (\mathbf{r}_{cm}|\psi_{cm}\rangle)\left(\langle\mathbf{r}'_1| \otimes \cdots \otimes \langle\mathbf{r}'_{N-1}|\psi_{rel}\rangle\right) \\ &= \psi_{cm}(\mathbf{r}_{cm})\psi_{rel}(\mathbf{r}'_1, \cdots, \mathbf{r}'_{N-1}).\end{aligned} \tag{4.69}$$

4.2.1 Two-Particle System

As an example, let us consider a system of two particles, with masses m_1 and m_2. Within the classical mechanics, it is possible to completely specify the three dimensional coordinates of two particles, $\mathbf{r}_1$ and $\mathbf{r}_2$, and their momenta, $\mathbf{p}_1$ and $\mathbf{p}_2$. For the general case where the two particles interact with each other, as was mentioned before, it is often best to separate the dynamics into those for the center of mass and relative coordinates.

For the two particles, the center of mass coordinate is

$$\mathbf{r}_{cm} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{M}, \tag{4.70}$$

where $M = m_1 + m_2$, and the relative coordinate is

$$\mathbf{r}_{rel} = \mathbf{r}_1 - \mathbf{r}_2. \tag{4.71}$$

The above two equations can be used to express $\mathbf{r}_1$ and $\mathbf{r}_2$ in terms of $\mathbf{r}_{cm}$ and $\mathbf{r}_{rel}$ as follows:

$$\mathbf{r}_1 = \mathbf{r}_{cm} + \frac{m_2}{M}\mathbf{r}_{rel}, \tag{4.72}$$

$$\mathbf{r}_2 = \mathbf{r}_{cm} - \frac{m_1}{M}\mathbf{r}_{rel}. \tag{4.73}$$

Taking the time derivative of the above two equations leads to

$$\frac{d\mathbf{r}_1}{dt} = \frac{d\mathbf{r}_{cm}}{dt} + \frac{m_2}{M}\frac{d\mathbf{r}_{rel}}{dt}, \tag{4.74}$$

$$\frac{d\mathbf{r}_2}{dt} = \frac{d\mathbf{r}_{cm}}{dt} - \frac{m_1}{M}\frac{d\mathbf{r}_{rel}}{dt}. \tag{4.75}$$

As a result,

$$\begin{aligned}
\frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} &= \frac{m_1}{2}\left(\frac{d\mathbf{r}_1}{dt}\right)^2 + \frac{m_2}{2}\left(\frac{d\mathbf{r}_2}{dt}\right)^2 \\
&= \frac{m_1}{2}\left[\left(\frac{d\mathbf{r}_{cm}}{dt}\right)^2 + 2\frac{m_2}{M}\left(\frac{d\mathbf{r}_{cm}}{dt}\right)\cdot\left(\frac{d\mathbf{r}_{rel}}{dt}\right) + \frac{m_2^2}{M^2}\left(\frac{d\mathbf{r}_{rel}}{dt}\right)^2\right] \\
&+ \frac{m_2}{2}\left[\left(\frac{d\mathbf{r}_{cm}}{dt}\right)^2 - 2\frac{m_1}{M}\left(\frac{d\mathbf{r}_{cm}}{dt}\right)\cdot\left(\frac{d\mathbf{r}_{rel}}{dt}\right) + \frac{m_1^2}{M^2}\left(\frac{d\mathbf{r}_{rel}}{dt}\right)^2\right]
\end{aligned}$$

$$= \frac{M}{2}\left(\frac{d\mathbf{r}_{cm}}{dt}\right)^2 + \frac{\mu}{2}\left(\frac{d\mathbf{r}_{rel}}{dt}\right)^2$$

$$= \frac{\mathbf{p}_{cm}^2}{2M} + \frac{\mathbf{p}_{rel}^2}{2\mu}, \tag{4.76}$$

where $\mu = m_1 m_2/M$, the reduced mass for the two particle system, and

$$\mathbf{p}_{cm} = M\frac{d\mathbf{r}_{cm}}{dt}, \tag{4.77}$$

$$\mathbf{p}_{rel} = \mu\frac{d\mathbf{r}_{rel}}{dt}. \tag{4.78}$$

Hamiltonian and Schrödinger Equation for Two Particles with Separable Relative Potential

If the potential energy is a sum of those for $\mathbf{r}_{cm}$ and $\mathbf{r}_{rel}$, namely, $V(\mathbf{r}_1, \mathbf{r}_2) = V_{cm}(\mathbf{r}_{cm}) + V_{rel}(\mathbf{r}_{rel})$, the total classical Hamiltonian for the two particles can be expressed as

$$H = H_{cm} + H_{rel} = \frac{\mathbf{p}_{cm}^2}{2M} + V_{cm}(\mathbf{r}_{cm}) + \frac{\mathbf{p}_{rel}^2}{2\mu} + V_{rel}(\mathbf{r}_{rel}). \tag{4.79}$$

For the quantum mechanical case, the Hamiltonian operator is obtained by replacing the position and momentum variables with operators as follows:

$$\hat{H} = \hat{H}_{cm} + \hat{H}_{rel} = \frac{\hat{\mathbf{p}}_{cm}^2}{2M} + V_{cm}(\hat{\mathbf{r}}_{cm}) + \frac{\hat{\mathbf{p}}_{rel}^2}{2\mu} + V_{rel}(\hat{\mathbf{r}}_{rel}). \tag{4.80}$$

Let us introduce $|\psi_{cm,E_{cm}}\rangle$ and $|\psi_{rel,E_{rel}}\rangle$, which are respectively eigenstates of $\hat{H}_{cm}$ and $\hat{H}_{rel}$ as follows:

$$\hat{H}_{cm}|\psi_{cm,E_{cm}}\rangle = E_{cm}|\psi_{cm,E_{cm}}\rangle, \tag{4.81}$$

$$\hat{H}_{rel}|\psi_{rel,E_{rel}}\rangle = E_{rel}|\psi_{rel,E_{rel}}\rangle. \tag{4.82}$$

Then, it is straightforward to show that $|\psi\rangle = |\psi_{cm,E_{cm}}\rangle \otimes |\psi_{rel,E_{rel}}\rangle$ is an eigenstate of $\hat{H} = \hat{H}_{cm} + \hat{H}_{rel}$ with eigenvalue $E_{cm} + E_{rel}$.

4.2.2 Normal Modes and Vibrational Spectroscopy of Polyatomic Molecules

For a diatomic molecule in the absence of any external potential, the Hamiltonian operator given by Eq. (4.79) reduces to

$$\hat{H} = \frac{\hat{\mathbf{p}}_{cm}^2}{2M} + \frac{\hat{\mathbf{p}}^2}{2\mu} + V_{rel}(\hat{\mathbf{r}}), \tag{4.83}$$

where, note that the subscript *rel* used for the position operator in the previous subsection has been dropped here for convenience. Thus, $\hat{\mathbf{r}}$ is the operator measuring the relative position vector of the two nuclei and $\hat{\mathbf{p}}$ is the corresponding momentum operator. As will become detailed in the next chapter, the kinetic energy operator for the relative motion of the nuclei $\hat{\mathbf{p}}^2/(2\mu)$ in the above equation can be divided into one dimensional motion along the radius and rotational motions that are specified by two independent angles. Thus, for the diatomic molecule represented by the above Hamiltonian, which have total of 6 degrees of freedom, there is only one vibrational degree of freedom.

For polyatomic molecules with more than two nuclei, there are more than one vibrational degrees of freedom. For linear molecules with N atoms, the number of vibrational degrees of freedom, $N_{vib} = 3N - 5$. This is because there are two rotational degrees of freedom in addition to three degrees of freedom for the translational motion of the center of mass. On the other hand, for nonlinear molecules, there are three rotational degrees of freedom. As a result, there are $N_{vib} = 3N - 6$ vibrational degrees of freedom.

Let us consider a polyatomic molecule with N_{vib} vibrational degrees of freedom and assume that it is possible[2] to identify N_{vib} orthogonal coordinates x_k's with $k = 1, \cdots, N_{vib}$, which represent vibrational displacements from the minimum potential energy. The kinetic energy term can still be expressed as a quadratic form involving time derivatives of these coordinates. In other words, it is assumed that the kinetic energy corresponding to vibrational motion can be expressed as $\sum_k (m_k/2)(dx_k/dt)^2$ and that the difference of the potential energy from its minimum value can be expanded as follows:

$$\begin{aligned}\Delta V &= V(x_1, \cdots, x_{N_{vib}}) - V(0, \cdots, 0) \\ &= \frac{1}{2}\sum_i \sum_j \left(\frac{\partial^2 V}{\partial x_i \partial x_j}\right) x_i x_j + \cdots \\ &= \frac{1}{2}\sum_i \sum_j f_{ij} x_i x_j + \cdots,\end{aligned} \tag{4.84}$$

[2] Actual procedure of identifying orthogonal vibrational coordinates for a general polyatomic molecule is nontrivial. For general description, see [29].

Given that the displacements x_k are sufficiently small, the potential energy can be approximated up to the second order and the classical Hamiltonian representing the vibrational motion of the molecule can be approximated as

$$H_{vib} = \sum_j \frac{1}{2} m_j \dot{x}_j^2 + \frac{1}{2} \sum_j \sum_k f_{jk} x_j x_k. \tag{4.85}$$

Let us introduce mass-weighted coordinates $q_j = \sqrt{m_j} x_j$. Then, the above Hamiltonian can be expressed as

$$H_{vib} = \sum_j \frac{1}{2} \dot{q}_j^2 + \frac{1}{2} \sum_j \sum_k \tilde{f}_{jk} q_j q_k, \tag{4.86}$$

where

$$\tilde{f}_{jk} = \frac{f_{jk}}{\sqrt{m_j m_k}}. \tag{4.87}$$

In Eq. (4.86), the potential energy term can be expressed as

$$\frac{1}{2} \sum_j \sum_k \tilde{f}_{jk} q_j q_k = \frac{1}{2} \mathbf{q}^T \tilde{\mathbf{F}} \mathbf{q}, \tag{4.88}$$

where $\mathbf{q}^T = (q_1 \cdots q_{N_{vib}})$, the transpose of a column vector $\mathbf{q}$ with the same elements, and

$$\tilde{\mathbf{F}} = \begin{pmatrix} \tilde{f}_{11} & \tilde{f}_{12} & \cdots & \tilde{f}_{1N_{vib}} \\ \tilde{f}_{21} & \tilde{f}_{22} & \cdots & \tilde{f}_{2N_{vib}} \\ \vdots & \vdots & \vdots & \vdots \\ \tilde{f}_{N_{vib}1} & \tilde{f}_{N_{vib}2} & \cdots & \tilde{f}_{N_{vib}N_{vib}} \end{pmatrix}. \tag{4.89}$$

Note that the above matrix is real and symmetric. This is called Hessian matrix and has N_{vib} real eigenvalues. Thus, one can find out N_{vib} eigenvectors of $\tilde{\mathbf{F}}$ such that

$$\tilde{\mathbf{F}} \mathbf{u}_k = \lambda_k \mathbf{u}_k, \ k = 1, \cdots, N_{vib}. \tag{4.90}$$

The above eigenvectors can be chosen to be normalized. In addition, the real symmetric nature of $\tilde{\mathbf{F}}$ makes the eigenvectors orthogonal to each other. Thus, the following property is satisfied.

$$\mathbf{u}_k^T \mathbf{u}_j = \delta_{jk}, \ j, k = 1, 2, \cdots, N_{vib}. \tag{4.91}$$

Now one can express $\mathbf{q}$ in terms of these eigenvectors as follows:

$$\mathbf{q} = Q_1\mathbf{u}_1 + Q_2\mathbf{u}_2 + \cdots + Q_{N_{vib}}\mathbf{u}_{N_{vib}}. \tag{4.92}$$

Then, due to the properties of Eqs. (4.90) and (4.91), Eq. (4.88) can be expressed as

$$\frac{1}{2}\mathbf{q}^T\tilde{\mathbf{F}}\mathbf{q} = \frac{1}{2}\sum_{j=1}^{N_{vib}} \lambda_j Q_j^2. \tag{4.93}$$

In the above expression, all λ_j's are positive because the above term is a quadratic expansion of the potential energy V with respect to its minimum. If, for example, λ_j is negative, the displacement of Q_j, while all others remain zero, can make the potential energy lower than the minimum, which is contradictory. Therefore, we can introduce ω_j such that

$$\lambda_j = \omega_j^2, \;\; j = 1, \cdots, N_{vib}. \tag{4.94}$$

Taking time derivative of Eq. (4.92), we find that

$$\dot{\mathbf{q}} = \dot{Q}_1\mathbf{u}_1 + \dot{Q}_2\mathbf{u}_2 + \cdots + \dot{Q}_{N_{vib}}\mathbf{u}_{N_{vib}}. \tag{4.95}$$

Then, due to the orthonormality condition, Eq. (4.91), the kinetic energy term in Eq. (4.86) can be expressed as

$$\sum_j \frac{1}{2}\dot{q}_j^2 = \frac{1}{2}\dot{\mathbf{q}}^T \cdot \dot{\mathbf{q}} = \frac{1}{2}\sum_j \dot{Q}_j^2. \tag{4.96}$$

Therefore, combining Eqs. (4.93), (4.94), and (4.96), the Hamiltonian can be expressed as

$$H_{vib} = \sum_j \frac{1}{2}\left(\dot{Q}_j^2 + \omega_j^2 Q_j^2\right) = \sum_j \frac{1}{2}\left(P_j^2 + \omega_j^2 Q_j^2\right), \tag{4.97}$$

where $P_j = \dot{Q}_j$. The displacement vector represented by each eigenvector $\mathbf{u}_k$ is called the *normal mode* of vibration and ω_j is the corresponding normal mode vibrational frequency. Thus, Eq. (4.97) shows that the quadratic expansion of the deviation of the potential energy from its minimum can be expressed as a sum of N_{vib} one dimensional harmonic oscillator Hamiltonians of independent normal modes.

Molecular Vibrational Hamiltonian as a Sum of Harmonic Oscillators for Normal Modes

Due to the independence of amplitude along the direction of each normal mode from others, one can view the vibrational motion of polyatomic molecules as being consisting of one dimensional normal modes. Therefore, the quantum mechanical Hamiltonian operator for the vibrational motion of the polyatomic molecule can be expressed as

$$\hat{H}_{vib} = \sum_j \frac{1}{2}\left(\hat{P}_j^2 + \omega_j^2 \hat{Q}_j^2\right). \tag{4.98}$$

Let us denote the eigenstate of the jth term of the above harmonic oscillator Hamiltonian with eigenvalue $\hbar\omega_j(v_j + 1/2)$ as $|v_j\rangle$. Namely,

$$\hat{H}_{vib,j}|v_j\rangle = \frac{1}{2}\left(\hat{P}_j^2 + \omega_j^2 \hat{Q}_j^2\right)|v_j\rangle = \hbar\omega_j\left(v_j + \frac{1}{2}\right)|v_j\rangle. \tag{4.99}$$

Then, we can define the direct product of these states as

$$|\psi_v\rangle = |v_1\rangle \otimes \cdots \otimes |v_{N_{vib}}\rangle. \tag{4.100}$$

It is easy to show that the above state is an eigenstate of the total vibrational Hamiltonian as follows:

$$\hat{H}_{vib}|\psi_v\rangle = E_{v_1,\cdots,v_{N_{vib}}}|\psi_v\rangle, \tag{4.101}$$

where

$$E_{v_1,\cdots,v_{N_{vib}}} = \sum_{j=1}^{N_{vib}} \hbar\omega_j\left(v_j + \frac{1}{2}\right). \tag{4.102}$$

At the same time, one can define the position state of normal coordinates as direct product of those for individual modes,

$$|\mathbf{Q}\rangle = |Q_1\rangle \otimes \cdots \otimes |Q_{N_{vib}}\rangle. \tag{4.103}$$

Then, the position representation of the eigenstate is given by the product of those for individual modes,

$$\psi_{vib}(\mathbf{Q}) = \langle \mathbf{Q}|\psi_v\rangle = \prod_{j=1}^{N_{vib}} \langle Q_j|v_j\rangle = \prod_{j=1}^{N_{vib}} \psi_{v_j}(Q_j). \tag{4.104}$$

Not all the vibrational normal modes can be detected by the IR spectroscopy and/or the Raman spectroscopy. As was mentioned in Chap. 3, only those modes for which dipole moment changes are IR active. On the other hand, vibrational modes for which the polarizability tensor changes with displacements are Raman active. There are vibrational modes that are not active either in IR or Raman, which are called silent modes. A systematic consideration of these vibrational modes is possible employing the group theory, which will be described in more detail in Chap. 9 where we consider overall molecular spectroscopy.

For each of IR and Raman active modes, the allowed transitions within the harmonic oscillator approximation correspond to

$$\Delta v_j = \pm 1, \tag{4.105}$$

where v_j is the vibrational quantum number for either IR or Raman active mode. For IR absorption, only $\Delta v_j = 1$ transition occurs. As was the case for diatomic molecule, the majority of these transitions are from the ground vibrational state ($v_j = 0$) to the first excited vibrational state ($v_j = 1$). For the Raman spectroscopy, $\Delta v_j = 1$ corresponds to Stokes transition and $\Delta v_j = -1$ corresponds to anti-Stokes transition. The Stokes transition is dominantly from the ground ($v_j = 0$) to the first excited state ($v_j = 1$), whereas the anti-Stokes transition is dominantly from the first excited vibration state ($v_j = 1$) to the ground vibrational state ($v_j = 0$). Relative intensities of Stokes and anti-Stokes peaks are determined by populations of initial states. Since thermal population of the first excited vibrational state is much smaller than that of the ground vibrational state for typical small to intermediate size molecules, intensities of Stokes peaks are much stronger than those of anti-Stokes peaks for these molecules.

4.3 Summary and Questions

Three dimensional position and momentum states can be defined as direct products of those for x, y, z components of the Cartesian coordinate system. Accordingly, all quantum mechanical operators, including the Hamiltonian, for a quantum particle in three dimensional space can be defined in the direct product space of those for the three dimensional position or momentum coordinates. Similarly, for a system of N interacting quantum particles, direct products of position and momentum states can be used to construct position and momentum states for the corresponding $3N$ dimensional position and momentum vectors. The resulting direct product space of position or momentum in turn can be used to represent any physical observables, including the Hamiltonian, of the many-particle quantum system for any kind of interacting potentials.

On the other hand, when it comes to finding analytical solutions for a general multidimensional Schrödinger equation, it is in general necessary to decompose the equation into those for one dimensional coordinates. The symmetry of a given

system plays an important role in such decomposition. For the case of a particle confined in a three dimensional rectangular box, it is possible to separate the equation into the sum of three independent terms for different Cartesian components and to assume that the wavefunction is given by a product form of those for the three components. For a three dimensional harmonic oscillator, a similar decomposition into each direction is possible. For these systems with multiple degrees of freedom, it is often the case that certain eigenstates have the same eigenvalue. These states are called degenerate and the number of states with the same eigenvalue is called the degeneracy of the eigenvalue.

Many particle systems in general can be described more conveniently by separating the center of mass coordinates and all other relative coordinates. This is the case for quantum many particle systems as well. For polyatomic molecules consisting of N atoms, the wavefunction representing the three dimensional center of mass motion can factor out as a simple free motion if there are no external potentials. After subtracting additional two (for linear molecule) or three degrees of freedom representing rotation, the Hamiltonian describing the pure vibrational motion can be identified.

Given that the potential energy for the multidimensional vibrational motion can be approximated up to the quadratic terms of the vibrational displacements around the potential minimum, it is possible to diagonalize the second derivative matrix of the potential energy, which is called Hessian matrix, resulting in normal vibrational modes. Each of these normal modes can be described as independent one dimensional vibrational motion, making it possible to reduce the quantum mechanical vibrational motion of polyatomic molecules as independent products of those for effectively one dimensional harmonic oscillators. Out of these normal modes, those that induce change in the dipole moment are IR active and those that induce change in the polarizability are Raman active.

Questions

- How can a direct product space be constructed to represent states of many quantum particles out of those for single particle states? Is the direct product space complete even though the particles are interacting with each other?
- Consider three dimensional position and momentum operators of a quantum particle. Given the components of these along two orthogonal directions, can they always be measured simultaneously with arbitrary precision?
- What does the degeneracy inform about the symmetry of a quantum system? Does the system have more degeneracy if it has more symmetry?
- What is the degeneracy of the first excited energy of a quantum particle confined in a cube?

(continued)

- When can the Scrödinger equation for a multidimensional system be solved by the separation of variables method?
- For a molecule with a nonzero net charge, can one use the center of mass coordinate system to define the dipole moment of the molecule uniquely?
- Why introducing a mass weighted coordinates is convenient for describing the vibrational motion of a polyatomic molecule in general?
- Is it possible for a certain vibrational normal mode of a polyatomic molecule to be active in neither IR nor Raman spectroscopy?

Exercise Problems with Solutions

4.1 A quantum state $|\psi\rangle$ represents a quantum particle in three dimensional space, and the corresponding wave function is as follows:

$$\langle \mathbf{r}|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}} \exp\{i\,(\mathbf{k}\cdot\mathbf{r})\} = \frac{1}{\sqrt{2\pi\hbar}} \exp\left\{i\,\left(k_x x + k_y y + k_z z\right)\right\},$$

where $\mathbf{k} = k_x\mathbf{e}_x + k_y\mathbf{e}_y + k_z\mathbf{e}_z$ is a constant three dimensional vector. Find out expressions for $\langle \mathbf{r}||\hat{\mathbf{r}}|^2|\psi\rangle$, $\langle \mathbf{r}||\hat{\mathbf{p}}|^2|\psi\rangle$, $\langle \mathbf{r}|(\hat{\mathbf{r}}\cdot\hat{\mathbf{p}} + \hat{\mathbf{p}}\cdot\hat{\mathbf{r}})|\psi\rangle$.

Solution 4.1 First, for $\langle \mathbf{r}||\hat{\mathbf{r}}|^2|\psi\rangle$,

$$\begin{aligned}\langle \mathbf{r}||\hat{\mathbf{r}}|^2|\psi\rangle &= (x^2+y^2+z^2)\langle \mathbf{r}|\psi\rangle \\ &= \frac{1}{2\pi\hbar}(x^2+y^2+z^2)e^{i(k_x x + k_y y + k_z z)}.\end{aligned}$$

For $\langle \mathbf{r}||\hat{\mathbf{p}}|^2|\psi\rangle$,

$$\begin{aligned}\langle \mathbf{r}||\hat{\mathbf{p}}|^2|\psi\rangle &= \langle \mathbf{r}|(\hat{p}_x^2+\hat{p}_y^2+\hat{p}_z^2)|\psi\rangle \\ &= -\hbar^2\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\langle \mathbf{r}|\psi\rangle \\ &= -\hbar^2\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\frac{1}{\sqrt{2\pi\hbar}}e^{i(k_x x + k_y y + k_z z)} \\ &= \hbar^2(k_x^2+k_y^2+k_z^2)\frac{1}{\sqrt{2\pi\hbar}}e^{i(k_x x + k_y y + k_z z)}.\end{aligned}$$

Finally, for $\langle \mathbf{r}|(\hat{\mathbf{r}}\cdot\hat{\mathbf{p}}+\hat{\mathbf{p}}\cdot\hat{\mathbf{r}})|\psi\rangle$,

$$\begin{aligned}
&\langle \mathbf{r}|(\hat{\mathbf{r}}\cdot\hat{\mathbf{p}}+\hat{\mathbf{p}}\cdot\hat{\mathbf{r}})|\psi\rangle \\
&= \frac{\hbar}{i}\left(x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}+\frac{\partial}{\partial x}x+\frac{\partial}{\partial y}y+\frac{\partial}{\partial z}z\right)\langle \mathbf{r}|\psi\rangle \\
&= \left(2\frac{\hbar}{i}\left(x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}\right)+3\frac{\hbar}{i}\right)\langle \mathbf{r}|\psi\rangle \\
&= \hbar\left(2(xk_x+yk_y+zk_z)-3i\right)\frac{1}{\sqrt{2\pi\hbar}}e^{i(k_x x+k_y y+k_z z)}.
\end{aligned}$$

4.2 A quantum state $|\psi\rangle$ represents a quantum particle in three dimensional space, and the corresponding wave function is as follows:

$$\langle \mathbf{r}|\psi\rangle = \left(\frac{\gamma}{\pi}\right)^{3/4}\exp\left\{-\frac{\gamma}{2}\left(x^2+y^2+z^2\right)\right\},$$

where γ is a constant real number. Find out expressions for $\langle \mathbf{r}||\hat{\mathbf{r}}|^2|\psi\rangle$, $\langle \mathbf{r}||\hat{\mathbf{p}}|^2|\psi\rangle$, $\langle \mathbf{r}|(\hat{\mathbf{r}}\cdot\hat{\mathbf{p}}+\hat{\mathbf{p}}\cdot\hat{\mathbf{r}})|\psi\rangle$.

Solution 4.2 First, for $\langle \mathbf{r}||\hat{\mathbf{r}}|^2|\psi\rangle$,

$$\begin{aligned}
\langle \mathbf{r}||\hat{\mathbf{r}}|^2|\psi\rangle &= (x^2+y^2+z^2)\langle \mathbf{r}|\psi\rangle \\
&= \left(\frac{\gamma}{\pi}\right)^{3/4}(x^2+y^2+z^2)e^{-\gamma(x^2+y^2+z^2)/2}.
\end{aligned}$$

For $\langle \mathbf{r}||\hat{\mathbf{p}}|^2|\psi\rangle$,

$$\begin{aligned}
&\langle \mathbf{r}||\hat{\mathbf{p}}|^2|\psi\rangle = -\hbar^2\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\langle \mathbf{r}|\psi\rangle \\
&= -\left(\frac{\gamma}{\pi}\right)^{3/4}\hbar^2\left(\frac{\partial}{\partial x}(-\gamma x)+\frac{\partial}{\partial y}(-\gamma y)+\frac{\partial}{\partial z}(-\gamma z)\right)e^{-\gamma(x^2+y^2+z^2)/2} \\
&= \left(\frac{\gamma}{\pi}\right)^{3/4}\hbar^2\left(3\gamma-\gamma^2(x^2+y^2+z^2)\right)e^{-\gamma(x^2+y^2+z^2)/2}.
\end{aligned}$$

Finally, for $\langle \mathbf{r}|(\hat{\mathbf{r}}\cdot\hat{\mathbf{p}}+\hat{\mathbf{p}}\cdot\hat{\mathbf{r}})|\psi\rangle$,

$$\begin{aligned}
&\langle \mathbf{r}|(\hat{\mathbf{r}}\cdot\hat{\mathbf{p}}+\hat{\mathbf{p}}\cdot\hat{\mathbf{r}})|\psi\rangle \\
&= \frac{\hbar}{i}\left(x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}+\frac{\partial}{\partial x}x+\frac{\partial}{\partial y}y+\frac{\partial}{\partial z}z\right)\langle \mathbf{r}|\psi\rangle
\end{aligned}$$

$$= \left(\frac{\gamma}{\pi}\right)^{3/4} \left(2\frac{\hbar}{i}\left(x\frac{\partial}{\partial x} + y\frac{\partial}{\partial y} + z\frac{\partial}{\partial z}\right) - 3\hbar i\right) e^{-\gamma(x^2+y^2+z^2)/2}$$

$$= \left(\frac{\gamma}{\pi}\right)^{3/4} \left(2i\hbar\gamma(x^2 + y^2 + z^2) - 3i\hbar\right) e^{-\gamma(x^2+y^2+z^2)/2}.$$

4.3 For an electron confined in a three dimensional box, for which the lengths of three sides are 1.00, 2.00, and 3.00 nm, calculate the ground state, first excited, and second excited energies. Determine the degeneracy for each state.

Solution 4.3 Let us introduce $l = 1.00$ nm, and denote the three sides of the box as $a = l$, $b = 2l$, $c = 3l$. Let us also denote the mass of electron as $m_e = 9.109 \times 10^{-31}$ kg. Then, the energy eigenvalue of the electron in the three dimensional box is given by the following expression:

$$E_n = \frac{\hbar^2\pi^2}{2m_e l^2}\left(n_x^2 + \frac{n_y^2}{4} + \frac{n_z^2}{9}\right), \; n_x, n_y, n_z = 1, 2, 3, \ldots.$$

Below is the table of four lowest possible values of the sum within the parenthesis in the above equation.

n_x	n_y	n_z	$n_x^2 + n_y^2/4 + n_z^2/9$
1	1	1	$1 + 1/4 + 1/9 = 49/36$
1	1	2	$1 + 1/4 + 4/9 = 61/36$
1	2	1	$1 + 4/4 + 1/9 = 76/36$
1	1	3	$1 + 1/4 + 9/9 = 81/36$

On the other hand,

$$\frac{\hbar^2\pi^2}{2m_e l^2} = \frac{(1.055 \times 10^{-34})^2 \cdot 3.14^2}{2 \cdot 9.109 \times 10^{-31} \cdot (1.00 \times 10^{-9})^2} \text{ J} = 6.02 \times 10^{-20} \text{ J}.$$

Combining this value with the table, we find that $E_g = 8.19 \times 10^{-20}$J $= 0.511$ eV, $E_{ex-1} = 10.20 \times 10^{-20}$ J $= 0.637$ eV, and $E_{ex-2} = 12.71 \times 10^{-20}$ J $= 0.7933$ eV. None of these three states is degenerate. So, the degeneracy of each state is 1.

4.4 For an electron confined in a three dimensional box, for which two sides have the same length of 1.00 nm, and the remaining side has 2.00 nm, calculate the ground state, first excited state, and the second excited energies. Determine the degeneracy for each sate.

Solution 4.4 Using the same definition of l and m_e as in **Solution 4.3**, the energy eigenvalue for the present case becomes

$$E_n = \frac{\hbar^2\pi^2}{2m_e l^2}\left(n_x^2 + n_y^2 + \frac{n_z^2}{4}\right).$$

The table for the lowest possible four values of the sum within the parenthesis in the above equation is as follows.

n_x	n_y	n_z	$n_x^2 + n_y^2/4 + n_z^2/9$
1	1	1	$1+1+1/4 = 9/4$
1	1	2	$1+1+1 = 3$
1	1	3	$1+1+9/4 = 17/4$
2	1	1	$4+1+1/4 = 21/4$
1	2	1	$1+4+1/4 = 21/4$

Therefore, $E_g = 13.5\times10^{-20}$ J $= 0.843$ eV, $E_{ex-1} = 18.1\times10^{-20}$ J $= 1.13$ eV, and $E_{ex-2} = 25.6 \times 10^{-20}$ J $= 1.60$ eV. None of these three states is degenerate. So, the degeneracy of each state of the three states is 1. As can be seen from the table above, the degeneracy appears in the third excited state.

4.5 A quantum particle with unit mass ($m = 1$) is subject to the following potential energy.

$$V(\mathbf{r}) = \begin{cases} \frac{1}{2}\omega^2 z^2, & 0 < x < a,\ 0 < y < a \\ \infty, & \text{otherwise} \end{cases},$$

where the angular frequency ω and a are related by $a^2\omega = 2\pi^2\hbar$. What is the ground state energy and wavefunction of this particle? What is the first excited state energy of this particle and its degeneracy? Find out all the degenerate eigenfunctions for the first excited state.

Solution 4.5 The Schrödinger equation for the wavefunction for $0 < x < a$ and $0 < y < a$ is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(x, y, z) + \frac{1}{2}m\omega^2 z^2\psi(x, y, z) = E\psi(x, y, z).$$

For other regions, the wavefunction is zero. Through separation of variables, this can be solved with

$$\psi_{n_x,n_y,v}(x, y, z) = \frac{2}{a}\sin\left(\frac{\pi n_x x}{a}\right)\sin\left(\frac{\pi n_y y}{a}\right)\psi_v(z),$$

where $n_x, n_y = 1, 2, \cdots, v = 0, 1, 2, \cdots$, and

$$\psi_v(z) = N_v e^{-\gamma z^2/2} H_v(\sqrt{\gamma} z),$$

with $\gamma = m\omega/\hbar$. The corresponding eigenvalue is

$$E_{n_x,n_y,v} = \frac{\pi^2\hbar^2}{2a^2}\left(n_x^2 + n_y^2\right) + \hbar\omega(v + \frac{1}{2}).$$

Since $a^2 = 2\pi^2\hbar/\omega$ as assumed, the following relation holds:

$$\frac{\pi^2\hbar^2}{2a^2} = \frac{\hbar\omega}{4}.$$

Therefore,

$$E_{n_x,n_y,v} = \frac{\hbar\omega}{4}(n_x^2 + n_y^2) + \hbar\omega(v + \frac{1}{2}).$$

The ground state energy and the wavefunction is for $n_x = n_y = 1$ and $v = 0$ as follows:

$$E_{1,1,0} = \frac{\hbar\omega}{4}(1+1) + \frac{\hbar\omega}{2} = \hbar\omega,$$

$$\psi_{110}(x, y, z) = \frac{2}{a}\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{\pi y}{b}\right)\psi_0(z).$$

The first excited state energy is for $n_x = 2, n_y = 1, v = 0$ or for $n_x = 1, n_y = 2, v = 0$ as follows:

$$E_{2,1,0} = E_{1,2,0} = \frac{5\hbar\omega}{4} + \frac{\hbar\omega}{2} = \frac{7\hbar\omega}{4},$$

for which the two degenerate wavefunctions are

$$\psi_{210}(x, y, z) = \frac{2}{a}\sin\left(\frac{2\pi x}{a}\right)\sin\left(\frac{\pi y}{b}\right)\psi_0(z),$$

$$\psi_{120}(x, y, z) = \frac{2}{a}\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi y}{b}\right)\psi_0(z).$$

4.6 For each of the molecule, determine the number of vibrational degrees of freedom, and draw pictures of all IR inactive modes.

(a) Carbonyl-sulfide (OCS)
(b) Acetylene (C_2H_2, linear form in the ground state)
(c) Phosphine (PH_3)
(d) Cyclopropenylidene (C_3H_2)

Solution 4.6 Answers (except for the pictures of IR active modes) for each case are provided below.

(a) This is a linear molecular. Therefore, there are $9 - 5 = 4$ vibrational modes. There are no IR inactive modes. In other words, all vibrational modes are IR active. This is because all vibrational normal modes change the dipole moments of the molecule in one way or the other.
(b) This is a linear molecule. Therefore, there are $12 - 5 = 7$ vibrational modes. Out of these, there are two symmetric stretching vibrational modes, which are IR inactive.
(c) This is a nonlinear molecule. Therefore, there are $12-6 = 6$ vibrational modes. There are no IR inactive modes. In other words, all vibrational modes change dipole moments and are IR active.
(d) There are $15 - 6 = 9$ vibrational modes. All vibrational normal modes change the dipole moment of the molecule. Therefore, there are no IR inactive modes.

4.7 A molecule has three vibrational degrees of freedom, and thus its vibration involves three mass-weighted vibrational coordinates q_1, q_2, and q_3. The vibrational potential energy is zero for $q_1 = q_2 = q_3 = 0$ and the potential energy can be expressed as a quadratic function of these coordinates. The mass-weighted Hessian matrix for these coordinates is given by

$$\tilde{\mathbf{F}} = \omega^2 \begin{pmatrix} 1 & \frac{1}{2\sqrt{2}} & 0 \\ \frac{1}{2\sqrt{2}} & 1 & \frac{1}{2\sqrt{2}} \\ 0 & \frac{1}{2\sqrt{2}} & 1 \end{pmatrix}.$$

Answer the following questions.

(a) Express the total vibrational potential energy in terms of q_1, q_2, and q_3.
(b) Find out the three normal mode vibrational frequencies of the molecule (expressed in terms of ω).
(c) Determine the three normal mode vectors.

Solution 4.7 Let us introduce $\mathbf{u}_1^T = (1, 0, 0)$, $\mathbf{u}_2^T = (0, 1, 0)$, and $\mathbf{u}_3^T = (0, 0, 1)$, where subscript T denotes transpose. Then, $\mathbf{q}^T = (q_1, q_2, q_3) = q_1\mathbf{u}_1^T + q_2\mathbf{u}_2^T + q_3\mathbf{u}_3^T$ and $\mathbf{q} = q_1\mathbf{u}_1 + q_2\mathbf{u}_2 + q_3\mathbf{u}_3$.

(a) The vibrational potential energy can be expressed as follows:

$$\begin{aligned}V(q_1, q_2, q_3) &= \frac{1}{2}\mathbf{q}^T\tilde{\mathbf{F}}\mathbf{q} \\ &= \frac{\omega^2}{2}\left(q_1^2 + \frac{q_1q_2}{2\sqrt{2}} + \frac{q_1q_2}{2\sqrt{2}} + q_2^2 + \frac{q_3q_2}{2\sqrt{2}} + \frac{q_2q_3}{2\sqrt{2}} + q_3^2\right) \\ &= \frac{\omega^2}{2}\left(q_1^2 + q_2^2 + q_3^2 + \frac{1}{\sqrt{2}}q_1q_2 + \frac{1}{\sqrt{2}}q_2q_3\right).\end{aligned}$$

(b) The normal mode frequencies can be obtained from the eigenvalues of $\tilde{\mathbf{F}}$, which can be obtained from the following equation:

$$\begin{vmatrix} 1-\lambda & \frac{1}{2\sqrt{2}} & 0 \\ \frac{1}{2\sqrt{2}} & 1-\lambda & \frac{1}{2\sqrt{2}} \\ 0 & \frac{1}{2\sqrt{2}} & 1-\lambda \end{vmatrix} = (1-\lambda)\left(\frac{3}{2}-\lambda\right)\left(\frac{1}{2}-\lambda\right) = 0.$$

Thus, the solutions are $\lambda = 1/2, 1, 3/2$. Since the values of this multiplied by ω^2 are squares of the normal mode frequencies, the resulting three normal mode frequencies are $\omega/\sqrt{2}$, ω, and $\omega\sqrt{3/2}$, which will be denoted as ω_a, ω_b, and ω_c here.

(c) The normal modes can be determined by plugging the eigenvalues to the eigenvalue equation. For $\lambda = 1/2$,

$$\begin{pmatrix} 1 & \frac{1}{2\sqrt{2}} & 0 \\ \frac{1}{2\sqrt{2}} & 1 & \frac{1}{2\sqrt{2}} \\ 0 & \frac{1}{2\sqrt{2}} & 1 \end{pmatrix}\begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix}.$$

Solving the above equation, we obtain $Q_1 = Q_3 = -Q_2/\sqrt{2}$. Using the normalization condition, $Q_1 = 1/2$, $Q_2 = -1/\sqrt{2}$, and $Q_3 = 1/2$. Thus, for $\omega_a = \omega/\sqrt{2}$, the normal mode is as follows:

$$\mathbf{Q}_a = \frac{1}{2}\mathbf{u}_1 - \frac{1}{\sqrt{2}}\mathbf{u}_2 + \frac{1}{2}\mathbf{u}_3.$$

For $\lambda = 1$,

$$\begin{pmatrix} 1 & \frac{1}{2\sqrt{2}} & 0 \\ \frac{1}{2\sqrt{2}} & 1 & \frac{1}{2\sqrt{2}} \\ 0 & \frac{1}{2\sqrt{2}} & 1 \end{pmatrix}\begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix} = \begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix}.$$

Solving the above equation, we obtain $Q_1 = -Q_3$ and $Q_2 = 0$. Using the normalization condition, $Q_1 = 1/\sqrt{2}$ and $Q_3 = -1/\sqrt{2}$. Thus, for $\omega_b = \omega$, the normal mode is as follows:

$$\mathbf{Q}_b = \frac{1}{\sqrt{2}}(\mathbf{u}_1 - \mathbf{u}_3).$$

Finally, for $\lambda = 3/2$,

$$\begin{pmatrix} 1 & \frac{1}{2\sqrt{2}} & 0 \\ \frac{1}{2\sqrt{2}} & 1 & \frac{1}{2\sqrt{2}} \\ 0 & \frac{1}{2\sqrt{2}} & 1 \end{pmatrix} \begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix} = \frac{3}{2} \begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix}.$$

Solving the above equation, we obtain $Q_1 = Q_3 = Q_2/\sqrt{2}$. Using the normalization condition, $Q_1 = Q_3 = 1/2$ and $Q_2 = 1/\sqrt{2}$. Thus, for $\omega_c = \omega\sqrt{3/2}$, the normal mode is as follows:

$$\mathbf{Q}_c = \frac{1}{2}\mathbf{u}_1 + \frac{1}{\sqrt{2}}\mathbf{u}_2 + \frac{1}{2}\mathbf{u}_3.$$

Problems

4.8 A quantum state $|\psi\rangle$ represents a quantum particle in three dimensional space, and the corresponding wave function is

$$\langle \mathbf{r}|\psi\rangle = \left(\frac{\gamma}{\pi}\right)^{3/4} \exp\left\{-\frac{\gamma}{2}\left(x^2 + y^2 + z^2\right) + ik(x + y + z)\right\},$$

where γ is a constant real number. Find out expressions for $\langle \mathbf{r}||\hat{\mathbf{p}}|^2|\psi\rangle$ and $\langle \mathbf{r}|(\hat{\mathbf{r}} \cdot \hat{\mathbf{p}} + \hat{\mathbf{p}} \cdot \hat{\mathbf{r}})|\psi\rangle$.

4.9 For a proton confined in a three dimensional box, for which one side has length of 2.00 nm, and the remaining sides are 4.00 nm long, calculate the ground state, first excited state, and the second excited energies. Determine the degeneracy for each sate.

4.10 A quantum particle with unit mass ($m = 1$) is subject to the following potential energy.

$$V(\mathbf{r}) = \begin{cases} \frac{1}{2}\omega^2(y^2 + z^2), & 0 < x < a \\ \infty, & \text{otherwise} \end{cases},$$

Find out the general expression for the energy eigenvalue for this quantum particle. Determine the relationship between a and ω for the first excited state to have degeneracy of 3.

4.11 A quantum particle with unit mass ($m = 1$) is subject to the following potential energy. $V(\mathbf{r}) = 2(x^2 + y^2 + 4z^2)$. What is the ground state energy? What is the second excited state energy and its degeneracy?

4.12 A quantum particle with unit mass ($m = 1$) is subject to the following potential energy.

$$V(\mathbf{r}) = \frac{1}{2}\omega^2(x^2 + 4y^2 + 9z^2),$$

The eigenstate is represented as $|v_x, v_y, v_z\rangle$, where $v_x, v_y, v_z = 0, 1, 2, \cdots$.

(a) What is the ground state energy?
(b) What is the third excited state energy and its degeneracy? List all the corresponding degenerate states.

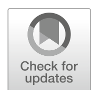
4.13 A molecule has three vibrational degrees of freedom, and thus its vibration involves three mass-weighted vibrational coordinates q_1, q_2, and q_3. The vibrational potential energy is zero for $q_1 = q_2 = q_3 = 0$ and the potential energy can be expressed as a quadratic function of these coordinates. The mass-weighted Hessian matrix for these coordinates is given by

$$\tilde{\mathbf{F}} = \omega^2 \begin{pmatrix} 2 & 1 & 1 \\ 1 & 2 & 0 \\ 1 & 0 & 2 \end{pmatrix}.$$

Answer the following questions.

(a) Express the total vibrational potential energy in terms of q_1, q_2, and q_3.
(b) Find out the three normal mode vibrational frequencies of the molecule (expressed in terms of ω).
(c) Determine the three normal mode vectors.

Chapter 5
Rotational States and Spectroscopy



What we observe is not nature itself but nature exposed to our method of questioning.

– Werner Heisenberg

Abstract This chapter describes rotational motion in two and three dimensions and solutions of time independent Schrödinger equations for corresponding rotational Hamiltonians. Detailed description of coordinate transformation is provided. It is shown that the periodic nature of rotational motion and the requirement that wavefunctions are uniquely determined and remain bounded leads to quantization of rotational energies. Well known spherical harmonics are shown to be eigenfunctions of angular momentum operators as well as three dimensional rotational Hamiltonian. These solutions are then used for the description of rotational motion of diatomic molecules as free rigid rotors. Important principles concerning pure rotational transitions and those accompanying vibrational transitions are explained. Corrections for rigid rotor states, incorporating the effects of centrifugal distortion and ro-vibrational coupling, are provided as well.

Rotation is intrinsically periodic motion along a curved and closed loop in space, and can be described best in coordinate systems different from Cartesian coordinates. In two dimensions, this can be done by introducing an angle variable in polar coordinate system. In three dimension, it takes consideration of two angle variables in the spherical coordinate system.

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5.1 Rotation in Two Dimensional Space

Let us consider a classical particle that moves with constant speed on a circle of radius r centered at origin in a two dimensional xy-plane as shown in Fig. 5.1. The classical Hamiltonian for such a motion is

$$H_R = \left.\frac{p^2}{2m}\right|_{r=\sqrt{x^2+y^2}} = \left.\frac{1}{2m}(p_x^2 + p_y^2)\right|_{r=\sqrt{x^2+y^2}}, \tag{5.1}$$

where $r = \sqrt{x^2 + y^2}$ in the subscript implies that it remains constant throughout the motion. Without this constraint, the quantum mechanical Hamiltonian operator corresponding to the above classical Hamiltonian is

$$\hat{H}_f = \frac{1}{2m}\left(\hat{p}_x^2 + \hat{p}_y^2\right), \tag{5.2}$$

which is in fact the Hamiltonian for free motion as the subscript f indicates. In order to represent the rotational motion, it should be possible to impose the constraint of fixed $r = \sqrt{x^2 + y^2}$. For the specification of this constraint, it is important to use an appropriate coordinate system as will become clear below.

Let us first denote the quantum mechanical rotational Hamiltonian as $\hat{H}_R$ and start with the time independent Schrödinger equation in the Dirac notation.

$$\hat{H}_R|\psi\rangle = E_R|\psi\rangle. \tag{5.3}$$

The position representation of this is obtained by taking the inner product with $\langle x, y| \equiv \langle x| \otimes \langle y|$, the bra representing the state with cartesian coordinates x and y.

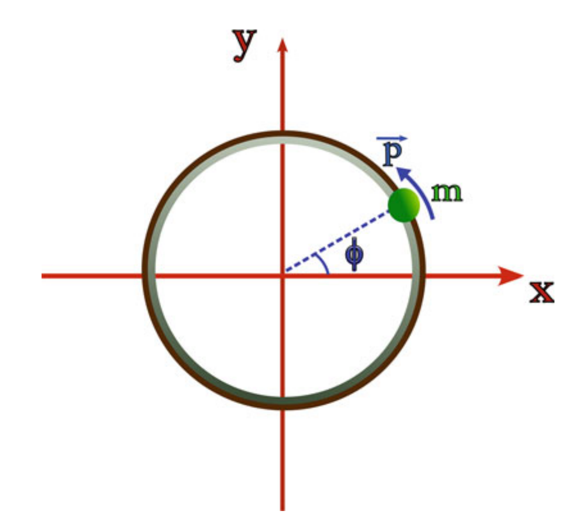


Fig. 5.1 Illustration of a two dimensional (in the xy-plane) rotation (around the z axis)

Namely, the Schrödinger equation for the waefunction $\psi(x, y) = \langle x, y|\psi\rangle$ is given by

$$\langle x, y|\hat{H}_R|\psi\rangle = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\psi(x, y)\Big|_{r=\sqrt{x^2+y^2}}$$
$$= E_R\psi(x, y)\Big|_{r=\sqrt{x^2+y^2}}, \tag{5.4}$$

where E_R is the eigenvalue for the rotational energy to be determined.

Equation (5.4) appears to be complicated due to the constraint. However, converting (x, y) to polar coordinates simplifies the mathematical problem significantly. Let us consider polar coordinates in the two dimensional plane, (r, ϕ), which are defined by

$$r = \sqrt{x^2 + y^2}, \tag{5.5}$$

$$\tan\phi = \frac{y}{x}. \tag{5.6}$$

Given the above values, any cartesian coordinates can be determined by $x = r\cos\phi$ and $y = r\sin\phi$.

Employing the chain rule for differentiation, the partial derivatives with respect x and y can be related to those of r and ϕ as follows:

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial\phi}{\partial x}\frac{\partial}{\partial\phi}, \tag{5.7}$$

$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial\phi}{\partial y}\frac{\partial}{\partial\phi}. \tag{5.8}$$

From Eq. (5.5), we find that

$$\frac{\partial r}{\partial x} = \frac{x}{\sqrt{x^2 + y^2}} = \frac{x}{r} = \cos\phi, \tag{5.9}$$

$$\frac{\partial r}{\partial y} = \frac{y}{\sqrt{x^2 + y^2}} = \frac{y}{r} = \sin\phi. \tag{5.10}$$

From Eq. (5.6), we also find that

$$\sec^2\phi\frac{\partial\phi}{\partial x} = -\frac{y}{x^2}, \tag{5.11}$$

$$\sec^2\phi\frac{\partial\phi}{\partial y} = \frac{1}{x}. \tag{5.12}$$

Note that $\sec^2\phi = 1 + \tan^2\phi = r^2/x^2$. Thus, the above identities can be simplified to

$$\frac{\partial\phi}{\partial x} = -\frac{y}{r^2} = -\frac{\sin\phi}{r}, \tag{5.13}$$

$$\frac{\partial\phi}{\partial y} = \frac{x}{r^2} = \frac{\cos\phi}{r}. \tag{5.14}$$

Combining Eqs. (5.9), (5.10), (5.13), and (5.14) with Eqs. (5.7) and (5.8), we find that

$$\frac{\partial}{\partial x} = \cos\phi\frac{\partial}{\partial r} - \frac{\sin\phi}{r}\frac{\partial}{\partial\phi}, \tag{5.15}$$

$$\frac{\partial}{\partial y} = \sin\phi\frac{\partial}{\partial r} + \frac{\cos\phi}{r}\frac{\partial}{\partial\phi}. \tag{5.16}$$

The above two identities can be combined to express the sum of squared partial derivatives in Eq. (5.4) as follows:

$$\begin{aligned}
\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} &= \left(\cos\phi\frac{\partial}{\partial r} - \frac{\sin\phi}{r}\frac{\partial}{\partial\phi}\right)\left(\cos\phi\frac{\partial}{\partial r} - \frac{\sin\phi}{r}\frac{\partial}{\partial\phi}\right) \\
&+ \left(\sin\phi\frac{\partial}{\partial r} + \frac{\cos\phi}{r}\frac{\partial}{\partial\phi}\right)\left(\sin\phi\frac{\partial}{\partial r} + \frac{\cos\phi}{r}\frac{\partial}{\partial\phi}\right) \\
&= \cos^2\phi\frac{\partial^2}{\partial r^2} - \frac{\sin\phi}{r}\frac{\partial}{\partial\phi}\left(\cos\phi\frac{\partial}{\partial r}\right) \\
&\quad - \cos\phi\frac{\partial}{\partial r}\left(\frac{\sin\phi}{r}\frac{\partial}{\partial\phi}\right) + \frac{\sin\phi}{r}\frac{\partial}{\partial\phi}\left(\frac{\sin\phi}{r}\frac{\partial}{\partial\phi}\right) \\
&\quad + \sin^2\phi\frac{\partial^2}{\partial r^2} + \frac{\cos\phi}{r}\frac{\partial}{\partial\phi}\left(\sin\phi\frac{\partial}{\partial r}\right) \\
&\quad + \sin\phi\frac{\partial}{\partial r}\left(\frac{\cos\phi}{r}\frac{\partial}{\partial\phi}\right) + \frac{\cos\phi}{r}\frac{\partial}{\partial\phi}\left(\frac{\cos\phi}{r}\frac{\partial}{\partial\phi}\right) \\
&= (\cos^2\phi + \sin^2\phi)\frac{\partial^2}{\partial r^2} + \frac{1}{r}(\sin^2\phi + \cos^2\phi)\frac{\partial}{\partial r} \\
&\quad + \frac{1}{r^2}\left(\sin^2\phi + \cos^2\phi\right)\frac{\partial^2}{\partial\phi^2} \\
&= \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\phi^2} \\
&= \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r}\frac{\partial}{\partial\phi}\left(\frac{1}{r}\frac{\partial}{\partial\phi}\right).
\end{aligned} \tag{5.17}$$

The separation of differentials involving r and ϕ in Eq. (5.17) now makes it easy to impose constraint of constant r, which simply amounts to assuming that $\partial/\partial r = 0$. Thus, Eq. (5.4) simplifies to

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}\psi(x,y)\bigg|_{r=\sqrt{x^2+y^2}} = E_R\psi(x,y)|_{r=\sqrt{x^2+y^2}} . \tag{5.18}$$

Now, let us define

$$\psi_r(\phi) = \psi(x,y)|_{r=\sqrt{x^2+y^2}} , \tag{5.19}$$

and introduce $I = mr^2$, which is the moment of inertia for the rotational motion. Then, Eq. (5.18) becomes

$$-\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2}\psi_r(\phi) = E_R\psi_r(\phi). \tag{5.20}$$

A general solution of the above equation can be expressed as

$$\psi_r(\phi) = Ne^{im\phi}, \tag{5.21}$$

which results in the following relationship:

$$-\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2}\psi_r(\phi) = \frac{\hbar^2 m^2}{2I}\psi_r(\phi) = E_R\psi_r(\phi). \tag{5.22}$$

Equation (5.20) represents free motion along the ϕ coordinate. However, there is major difference of this rotational motion from that in infinite space. For the former, *the domain of ϕ representing different physical space is confined only to a range of* 2π. In other words, the periodic boundary condition, $\psi_r(\phi) = \psi_r(\phi + 2\pi)$, should be satisfied. This condition implies that

$$e^{im2\pi} = 1, \tag{5.23}$$

which can be satisfied only for integer values of $m = 0, \pm 1, \pm 2, \cdots$. Therefore, we obtain the following expression:

Eigenvalue of Two-Dimensional Rotation

$$E_{R,m} = \frac{\hbar^2 m^2}{2I} , m = 0, \pm 1, \pm 2, \cdots . \tag{5.24}$$

The normalization constant of the rotational wavefunction in Eq. (5.21) can be determined using the following condition:

$$\int_0^{2\pi} d\phi |\psi_r(\phi)|^2 = |N|^2 2\pi = 1. \tag{5.25}$$

A choice of $N = 1/\sqrt{2\pi}$ satisfies the above condition. Thus, the normalized eigenfunction of the 2-dimensional rotation with eigenvalue $m\hbar$ can be expressed as follows:

Normalized Eigenfunction of Two-Dimensional Rotation

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \; m = 0, \pm 1, \pm 2, \cdots \tag{5.26}$$

5.2 Rotation in Three Dimensional Space

The approach of obtaining rotational kinetic energy term directly from the Cartesian coordinate system for two-dimension can also be used for rotation in three dimensional space. For this, the spherical coordinate system, (r, θ, ϕ) (see Fig. 5.2), need to be used. This will be demonstrated in detail in the next section, when we describe angular momentum operators.

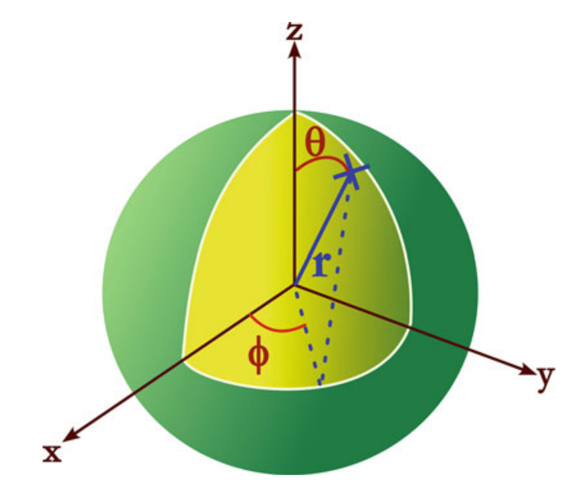


Fig. 5.2 Illustration of spherical coordinates (r, θ, ϕ)

Here, let us use a well-established formula for converting the Laplacian (∇^2) in the Cartesian coordinate system to that in a curvilinear coordinate system, where coordinates are defined along a system of three curved lines that remain orthogonal at each point. First, this can be illustrated for the two dimensional case given by Eq. (5.17).

For the polar coordinate system specified by (r, ϕ), the multiplicative factors used to convert the change in the values of coordinates to appropriate length units, so called the metric factors along r and ϕ, are respectively defined as $h_r = 1$ and $h_\phi = r$. Then, the Laplacian in the two dimensional space, Eq. (5.17), can be expressed as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{1}{h_r h_\phi}\frac{\partial}{\partial r}\left(\frac{h_\phi}{h_r}\frac{\partial}{\partial r}\right) + \frac{1}{h_r h_\phi}\frac{\partial}{\partial \phi}\left(\frac{h_r}{h_\phi}\frac{\partial}{\partial \phi}\right). \tag{5.27}$$

In fact, this is a special case of much more general expression that is valid in any dimension. For example, in three dimensional general coordinate system of (ξ_1, ξ_2, ξ_3) with metric factor along the three directions, h_1, h_2, and h_3, which themselves can be considered as functions of ξ_1, ξ_2, and ξ_3, there is a general expression [30] for the Laplacian as follows:

$$\begin{aligned}\nabla^2 &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\\ &= \frac{1}{h_1 h_2 h_3}\left\{\frac{\partial}{\partial \xi_1}\left(\frac{h_2 h_3}{h_1}\frac{\partial}{\partial \xi_1}\right) + \frac{\partial}{\partial \xi_2}\left(\frac{h_1 h_3}{h_2}\frac{\partial}{\partial \xi_2}\right) + \frac{\partial}{\partial \xi_3}\left(\frac{h_1 h_2}{h_3}\frac{\partial}{\partial \xi_3}\right)\right\}.\end{aligned} \tag{5.28}$$

In the above expression, $(1/h_i)(\partial/\partial\xi_i)$ for each of $i = 1, 2, 3$ corresponds to the component of the mathematical gradient vector operation and $(1/h_1 h_2 h_3)(\partial/\partial\xi_i)h_j h_k$ with $j \neq k \neq i$ corresponds to the divergence along each direction.

For the case of cartesian coordinate system, $h_x = h_y = h_z = 1$, which results in the simplest expression for ∇^2. However, for spherical coordinates (r, θ, ϕ) as shown in Fig. 5.2, $h_1 = 1$, $h_2 = r$, and $h_3 = r\sin\theta$. Therefore,

$$\begin{aligned}\nabla^2 &= \frac{1}{r^2\sin\theta}\left\{\frac{\partial}{\partial r}\left(r^2\sin\theta\frac{\partial}{\partial r}\right) + \frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right) + \frac{\partial}{\partial \phi}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\right)\right\}\\ &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial \phi^2}.\end{aligned} \tag{5.29}$$

For any function f, one can show that the derivative with respect to r above can be expressed as follows:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)f = \frac{2}{r}\frac{\partial}{\partial r}f + \frac{\partial^2}{\partial r^2}f = \frac{1}{r}\frac{\partial}{\partial r}f + \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right)f = \frac{1}{r}\frac{\partial^2}{\partial r^2}rf. \tag{5.30}$$

Employing this identity, Eq. (5.29) can often be expressed as

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}. \tag{5.31}$$

The above equation, or Eq. (5.29), now makes it easy to impose the constraint of fixed r and to represent the rotational motion of a particle with fixed r. In other words,

$$\begin{aligned} -\frac{-\hbar^2}{2m}\nabla^2\bigg|_r &= -\frac{\hbar^2}{2mr^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) \\ &= -\frac{\hbar^2}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right), \end{aligned} \tag{5.32}$$

where $I = mr^2$ has been defined as the moment of inertia for the case of two dimensional rotation and remains the same.

Let us denote the eigenfunction of a general three dimensional rotation as $Y(\theta, \phi)$. Then, the Schrödinger equation for this rotational motion is given by

$$-\frac{\hbar^2}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)Y(\theta,\phi) = EY(\theta,\phi). \tag{5.33}$$

Dividing the above equation with $-\hbar^2/(2I)$ and moving all terms to the lefthand side, we find that the above equation can be expressed as

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}Y(\theta,\phi)\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}Y(\theta,\phi) + \frac{2IE}{\hbar^2}Y(\theta,\phi) = 0. \tag{5.34}$$

Let us assume that $Y(\theta, \phi) = \Theta(\theta)\Phi_m(\phi)$, where $\Phi_m(\phi) = e^{im\phi}/\sqrt{2\pi}$, with $m = 0, \pm1, \pm2.\cdots$. Then,

$$\begin{aligned} &\frac{1}{\sin\theta}\Phi_m(\phi)\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\Theta(\theta)\right) + \frac{1}{\sin^2\theta}\Theta(\theta)\frac{d^2}{d\phi^2}\Phi_m(\phi) \\ &\quad + \frac{2IE}{\hbar^2}\Theta(\theta)\Phi_m(\phi) = 0. \end{aligned} \tag{5.35}$$

Since $\frac{d^2}{d\phi^2}\Phi_m(\phi) = -m^2\Phi_m(\phi)$, the above equation is simplified to

$$\Phi_m(\phi)\left[\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\Theta(\theta)\right) - \frac{m^2}{\sin^2\theta}\Theta(\theta) + \frac{2IE}{\hbar^2}\Theta(\theta)\right] = 0. \tag{5.36}$$

This implies that

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\Theta(\theta)\right)+\left(\beta-\frac{m^2}{\sin^2\theta}\right)\Theta(\theta)=0, \tag{5.37}$$

where

$$\beta=\frac{2IE}{\hbar^2}. \tag{5.38}$$

Equation (5.37) is called associated Legendre equation, for which well-known solutions exist. Appendix of this chapter provides a detailed consideration of this equation and show that well-defined physical solutions exist for the following conditions:

$$\beta=J(J+1),\, J=0,1,2,\cdots, \tag{5.39}$$

$$J\geq|m|. \tag{5.40}$$

The resulting solution for given J and m is called associated Legendre function and is denoted as $P_J^{|m|}(\cos\theta)$, for which detailed derivation is also provided in the Appendix.

Table 5.1 provides expressions for $P_J^{|m|}(\cos\theta)$ for small values of J and m. Plots of some Legendre polynomials ($m=0$) are shown in Fig. 5.3, and plots of associated Legendre polynomials for $J=4$ are shown in Fig. 5.4.

Table 5.1 Examples of associated Legendre functions

J	m	$P_J^m(x)$	$P_J^m(\cos\theta)$
0	0	1	1
1	0	x	$\cos\theta$
1	1	$(1-x^2)^{1/2}$	$\sin\theta$
2	0	$\frac{1}{2}(3x^2-1)$	$\frac{1}{2}(3\cos^2\theta-1)$
2	1	$3x(1-x^2)^{1/2}$	$3\cos\theta\sin\theta$
2	2	$3(1-x^2)$	$3\sin^2\theta$
3	0	$\frac{1}{2}(5x^3-3x)$	$\frac{1}{2}(5\cos^3\theta-3\cos\theta)$
3	1	$\frac{3}{2}(5x^2-1)(1-x^2)^{1/2}$	$\frac{3}{2}(5\cos^2\theta-1)\sin\theta$
3	2	$15x(1-x^2)$	$15\cos\theta\sin^2\theta$
3	3	$15(1-x^2)^{3/2}$	$15\sin^3\theta$
4	0	$\frac{1}{8}(35x^4-30x^2+3)$	$\frac{1}{8}(35\cos^4\theta-30\cos^2\theta+3)$
4	1	$\frac{5}{2}(7x^3-3x)(1-x^2)^{1/2}$	$\frac{5}{2}(7\cos^3\theta-3\cos\theta)\sin\theta$
4	2	$\frac{15}{2}(7x^2-1)(1-x^2)$	$\frac{15}{2}(7\cos^2\theta-1)\sin^2\theta$
4	3	$105x(1-x^2)^{3/2}$	$105\cos\theta\sin^3\theta$
4	4	$105(1-x^2)^2$	$105\sin^4\theta$

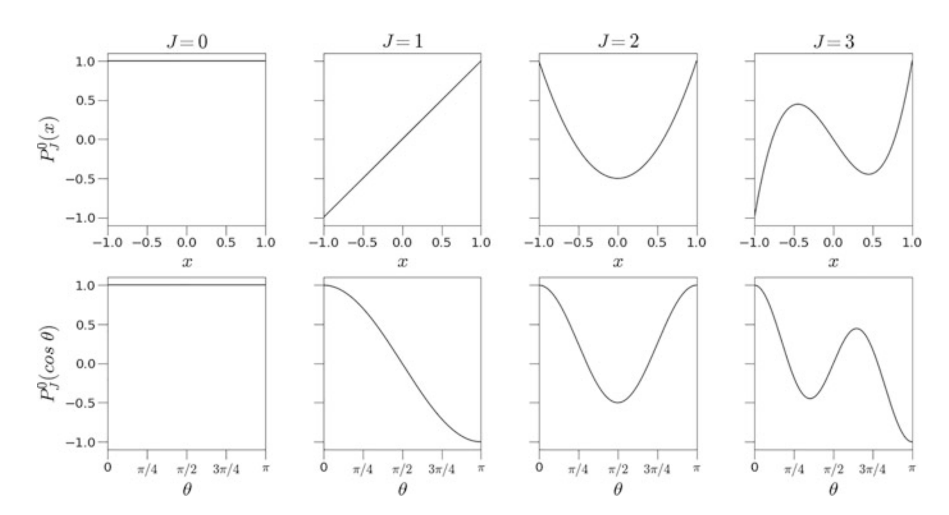


Fig. 5.3 Examples of four Legendre polynomials $P_J^0(x) = P_J^0(\cos\theta)$ for J=0, 1, 2, and 3. The upper panel is shown with respect to x and the lowe panel is shown with respect to θ. Normalizations for these plots were chosen so that $P_J^0(x) = 1$

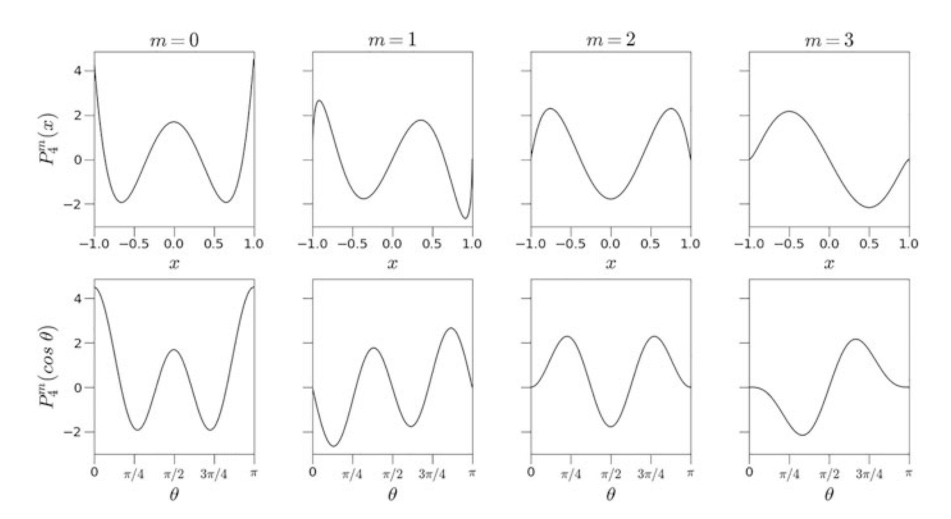


Fig. 5.4 Examples of four associated Legendre polynomials for $J = 4$, $P_4^m(x) = P_4^m(\cos\theta)$ with $m = 0$, 1, 2, and 3. The upper panel is with respect to $x = \cos\theta$ and the lower panel is with respect to θ

Each of $P_J^{|m|}(\theta)$, as can be seen from the examples in Table 5.1, is not normalized. Including normalization factor such that integration of the function over $d\cos\theta$ is equal to 1 and also now employing the appropriate subscript denoting the quantum numbers J and m, we can define

$$\Theta_J^m(\theta) = \left(\frac{2J+1}{2}\frac{(J-|m|)!}{(J+|m|)!}\right)^{1/2} P_J^{|m|}(\cos\theta). \quad (5.41)$$

Combining this with $\Phi_m(\phi)$, one can define eigenfunctions of the rotational Hamiltonian known as spherical Harmonics as follows.

Spherical Harmonics

$$Y_J^m(\theta,\phi) = i^{m+|m|}\left(\frac{2J+1}{4\pi}\frac{(J-|m|)!}{(J+|m|)!}\right)^{1/2} P_J^{|m|}(\cos\theta)e^{im\phi}, \quad (5.42)$$

where $i^{m+|m|}$ is the most commonly used phase factor although different phase factors are also used for convenience or other reasons. Expressions for some of these functions are provided in Table 5.2. Figure 5.5 provides plots of real and imaginary parts of these spherical harmonics for $J = 0$, 1, and 2.

Table 5.2 Expressions for spherical harmonics for $J = 0, \cdots, 3$

J	m	$Y_J^m(\theta,\phi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
1	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{\pm i\phi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
2	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\sin\theta\cos\theta e^{\pm i\phi}$
2	±2	$\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta e^{\pm 2i\phi}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta-3\cos\theta)$
3	±1	$\mp\left(\frac{21}{64\pi}\right)^{1/2}\sin\theta(5\cos^2\theta-1)e^{\pm i\phi}$
3	±2	$\left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta e^{\pm 2i\phi}$
3	±3	$\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta e^{\pm 3i\phi}$

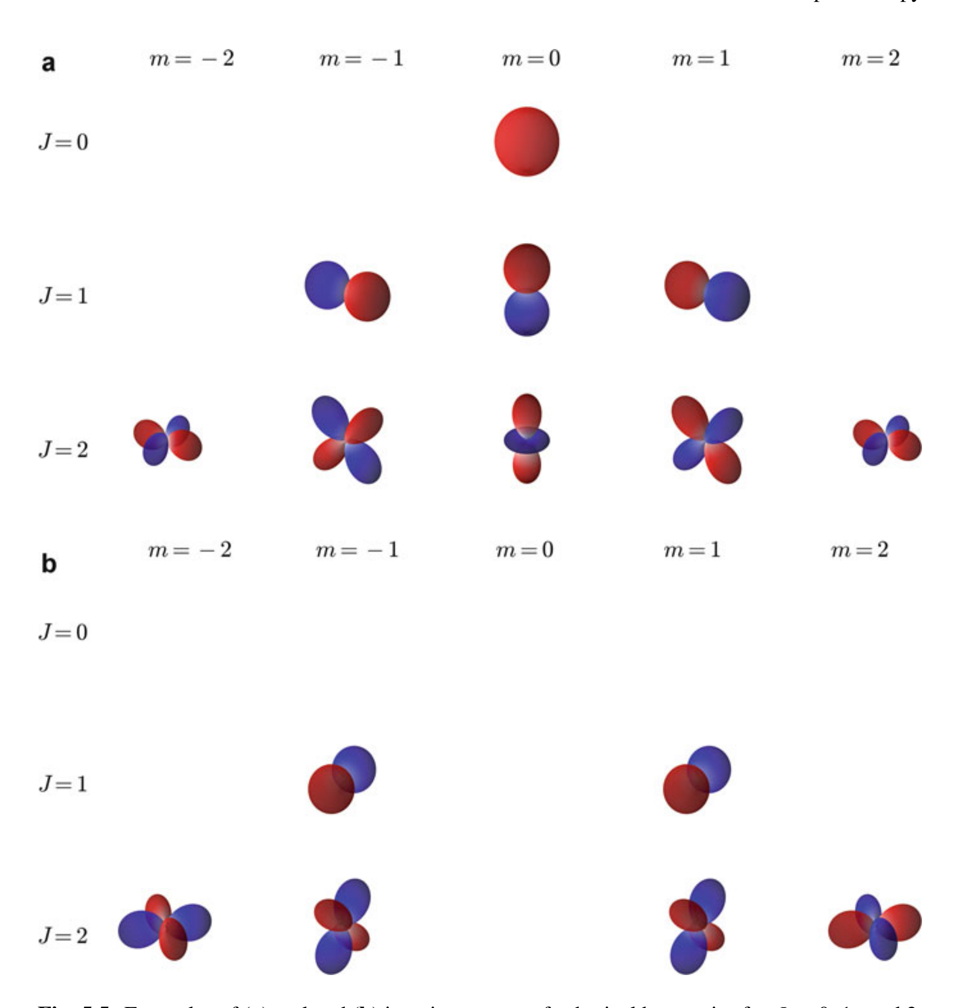


Fig. 5.5 Examples of (**a**) real and (**b**) imaginary parts of spherical harmonics for $J = 0, 1$, and 2

Combining Eqs. (5.38) and (5.39), we obtain the eigenvalue and eigenfunction of the three dimensional rotation as summarized below.

Eigenvalue and Eigenfunction of Three-Dimensional Rotation

The eigenvalue for a three-dimensional rotational motion with moment of inertia I is

$$E_J = \frac{\hbar^2}{2I} J(J+1), \tag{5.43}$$

(continued)

where $J = 0, 1, 2, \cdots$, and the corresponding eigenfunction, spherical harmonics, for each J and $m = 0, \cdots, \pm J$, satisfy the following time independent Schrödinger equation:

$$-\frac{\hbar^2}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)Y_J^m(\theta,\phi)=\frac{\hbar^2}{2I}J(J+1)Y_J^m(\theta,\phi). \tag{5.44}$$

In addition, since the dependence of $Y_J^m(\theta, \phi)$ on ϕ is only through $\Phi_m(\phi) = e^{im\phi}/\sqrt{2\pi}$, it is easy to show that

$$\frac{\hbar}{i}\frac{\partial}{\partial\phi}Y_J^m(\theta,\phi) = \hbar m Y_J^m(\theta,\phi). \tag{5.45}$$

Note that, for a given value of J, there are $2J+1$ possible values of m because

$$m = -J, \cdots, J. \tag{5.46}$$

The spherical harmonics defined by Eq. (5.42) satisfy the following normalization and orthogonality (orthonormality) condition:

$$\int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\,\phi Y_J^m(\theta,\phi)^* Y_{J'}^{m'}(\theta,\phi) = \delta_{JJ'}\delta_{mm'}. \tag{5.47}$$

The above identity in fact implies that $Y_J^m(\theta, \phi)$ form a complete orthonormal basis for any well-behaving functions depending on θ and ϕ. Namely, any function of θ and ϕ can be expressed as a linear combination of these as follows:

$$f(\theta,\phi) = \sum_{J,m} C_{J,m} Y_J^m(\theta,\phi), \tag{5.48}$$

where $C_{J,m}$'s can be determined uniquely using Eq. (5.47).

5.3 Angular Momentum Operators

Each of the spherical harmonics introduced in the previous section is an eigenfunction of the rotational part of the kinetic energy operator. In classical mechanics, such rotational energy can be expressed in terms of angular momentum. For example, consider a particle with mass m rotating with a constant speed v at a fixed distance

r from the origin. By introducing $L = mrv$, the kinetic energy of this particle can be expressed as

$$\frac{mv^2}{2} = \frac{L^2}{2mr^2} = \frac{L^2}{2I}. \tag{5.49}$$

In fact, the last expression for the rotational kinetic energy in the above equation is much more general and can be shown to be true if it is defined as the magnitude of the following angular momentum vector:

$$\begin{aligned} \mathbf{L} = \mathbf{r} \times \mathbf{p} &= L_x \mathbf{e}_x + L_y \mathbf{e}_y + L_z \mathbf{e}_z \\ &= (yp_z - zp_y)\mathbf{e}_x + (zp_x - xp_z)\mathbf{e}_y + (xp_y - yp_x)\mathbf{e}_z. \end{aligned} \tag{5.50}$$

The square of the magnitude of this vector can be shown to be

$$|\mathbf{L}|^2 = L_x^2 + L_y^2 + L_z^2 = r^2 p_\perp^2, \tag{5.51}$$

where $p_\perp$ is the projection of a momentum $\mathbf{p}$ vector to a plane perpendicular to $\mathbf{r}$. In other words, classically, kinetic energy can be decomposed as

$$T = \frac{|\mathbf{p}|^2}{2m} = \frac{p_\parallel^2 + p_\perp^2}{2m} = \frac{p_\parallel^2}{2m} + \frac{r^2 p_\perp^2}{2mr^2} = \frac{p_\parallel^2}{2m} + \frac{L^2}{2I}, \tag{5.52}$$

where $p_\parallel$ is the component of the momentum along the direction of $\mathbf{r}$. Thus, T can always be considered as the sum of the kinetic energy for a linear one-dimensional motion along the direction of $\mathbf{r}$ and rotational kinetic energy, which can be represented by the magnitude of the angular momentum vector $\mathbf{L}$ as

$$T_R = \frac{L^2}{2I} = \frac{1}{2I}\left(L_x^2 + L_y^2 + L_z^2\right). \tag{5.53}$$

Based on the above classical expression for the rotational kinetic energy, it is possible to define quantum mechanical Hamiltonian operator for three dimensional rotation as summarized below.

Hamiltonian for Three Dimensional Rotation

The Hamiltonian operator for a rotor with moment of inertia I can be expressed as

$$\hat{H}_R = \frac{\hat{L}^2}{2I} = \frac{1}{2I}\left(\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2\right), \tag{5.54}$$

(continued)

where $\hat{L}_k$'s, with $k = x, y$, and z, are cartesian components of angular momentum operators defined as

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \tag{5.55}$$

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z, \tag{5.56}$$

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x. \tag{5.57}$$

The three cartesian components of the angular momentum operators defined above do not commute with each other, unlike the linear momentum operators. Instead, the following relations hold.

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z, \tag{5.58}$$

$$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x, \tag{5.59}$$

$$[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y. \tag{5.60}$$

It is straightforward to prove the above identities for commutators of angular momentum operators using the identity of Eq. (2.57) or calculating the commutator directly. For example,

$$\begin{aligned}[\hat{L}_x, \hat{L}_y] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] \\ &= [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - [\hat{z}\hat{p}_y, \hat{z}\hat{p}_x] - [\hat{y}\hat{p}_z, \hat{x}\hat{p}_z] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] \\ &= \hat{y}[\hat{p}_z, \hat{z}]\hat{p}_x + \hat{x}[\hat{z}, \hat{p}_z]\hat{p}_y \\ &= i\hbar(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) = i\hbar\hat{L}_z. \end{aligned} \tag{5.61}$$

On the other hand, using the identities used above once again, one can prove that $\hat{L}^2$ commute with individual components, $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$. For example,

$$\begin{aligned}[\hat{L}^2, \hat{L}_z] &= [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_z] \\ &= \hat{L}_x[\hat{L}_x, \hat{L}_z] + [\hat{L}_x, \hat{L}_z]\hat{L}_x + \hat{L}_y[\hat{L}_y, \hat{L}_z] + [\hat{L}_y, \hat{L}_z]\hat{L}_y \\ &= \hat{L}_x(-i\hbar\hat{L}_y) + (-i\hbar\hat{L}_y)\hat{L}_x + \hat{L}_y(i\hbar\hat{L}_x) + (i\hbar\hat{L}_x)\hat{L}_y = 0. \end{aligned} \tag{5.62}$$

Results of application of the angular momentum operator components to the position bra $\langle \mathbf{r}|$ can be calculated by using those for position and momentum components as follows:

$$\langle \mathbf{r}|\hat{L}_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\langle \mathbf{r}|, \tag{5.63}$$

$$\langle \mathbf{r}|\hat{L}_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\langle \mathbf{r}|, \tag{5.64}$$

$$\langle \mathbf{r}|\hat{L}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\langle \mathbf{r}|. \tag{5.65}$$

In order to express these in terms of spherical coordinates, let us now consider conversion of Cartesian coordinates into spherical coordinates in more detail. First, the Cartesian components can be expressed in terms of spherical coordinates as follows:

$$x = r\sin\theta\cos\phi, \tag{5.66}$$

$$y = r\sin\theta\sin\phi, \tag{5.67}$$

$$z = r\cos\theta. \tag{5.68}$$

From these, one can also obtain expressions for spherical coordinates in terms of Cartesian coordinates as follows:

$$r = \sqrt{x^2 + y^2 + z^2}, \tag{5.69}$$

$$\tan\theta = \frac{\sqrt{x^2 + y^2}}{z}, \tag{5.70}$$

$$\tan\phi = \frac{y}{x}. \tag{5.71}$$

The above expression can be used to obtain the following relations between partial derivatives with respect to Cartesian coordinates and those with respect to spherical coordinates. First, the partial derivatives of r are expressed as

$$\frac{\partial r}{\partial x} = \frac{x}{\sqrt{x^2 + y^2 + z^2}} = \frac{r\sin\theta\cos\phi}{r} = \sin\theta\cos\phi, \tag{5.72}$$

$$\frac{\partial r}{\partial y} = \frac{y}{\sqrt{x^2 + y^2 + z^2}} = \frac{r\sin\theta\sin\phi}{r} = \sin\theta\sin\phi, \tag{5.73}$$

$$\frac{\partial r}{\partial z} = \frac{z}{\sqrt{x^2 + y^2 + z^2}} = \frac{r\cos\theta}{r} = \cos\theta. \tag{5.74}$$

The partial derivatives of θ, which can be obtained from the fact that $d\tan\theta = \sec^2\theta d\theta$, are given by

$$\frac{\partial\theta}{\partial x} = \cos^2\theta\frac{r\sin\theta\cos\phi}{r\sin\theta r\cos\theta} = \frac{\cos\theta\cos\phi}{r}, \tag{5.75}$$

$$\frac{\partial\theta}{\partial y} = \cos^2\theta\frac{r\sin\theta\sin\phi}{r\sin\theta r\cos\theta} = \frac{\cos\theta\sin\phi}{r}, \tag{5.76}$$

$$\frac{\partial\theta}{\partial z} = -\cos^2\theta\frac{r\sin\theta}{r^2\cos^2\theta} = -\frac{\sin\theta}{r}. \tag{5.77}$$

Finally, the partial derivatives of ϕ, which can be obtained from the fact that $d\tan\phi = \sec^2\phi d\phi$, can be expressed as

$$\frac{\partial\phi}{\partial x} = -\cos^2\phi\frac{r\sin\theta\sin\phi}{r^2\sin^2\theta\cos^2\phi} = -\frac{\sin\phi}{r\sin\theta}, \tag{5.78}$$

$$\frac{\partial\phi}{\partial y} = \cos^2\phi\frac{1}{r\sin\theta\cos\phi} = \frac{\cos\phi}{r\sin\theta}, \tag{5.79}$$

$$\frac{\partial\phi}{\partial z} = 0. \tag{5.80}$$

The above expressions can be used to convert the partial derivatives with respect to x, y, and z to those with respect to r, θ, and ϕ. The resulting expressions can then be used to obtain expressions for the components of angular momentum operator.

The expression for the angular momentum along the z-coordinate has the simplest form and can be shown to be

$$\begin{aligned}
\langle\mathbf{r}|\hat{L}_z &= \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\langle\mathbf{r}| \\
&= \frac{\hbar}{i}\left(r\sin\theta\cos\phi\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\right. \\
&\quad \left. - r\sin\theta\sin\phi\left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\right) \\
&= \frac{\hbar}{i}\frac{\partial}{\partial\phi}\langle\mathbf{r}|.
\end{aligned} \tag{5.81}$$

Considering the position state in spherical coordinate system, one can express $\langle\mathbf{r}|$ as follows:

$$\langle\mathbf{r}| = \langle r| \otimes \langle\theta| \otimes \langle\phi|. \tag{5.82}$$

The position ket $|\mathbf{r}\rangle$ can also be written in a similar way. Note that the ranges of these spherical coordinate variables are different from those of cartesian coordinates, and

are given by $0 \le r, 0 \le \theta \le \pi$, and $0 \le \phi < 2\pi$. Employing Eq. (5.82) in Eq. (5.81) and using the fact that $\langle r|$ and $\langle \theta|$ remain invariant after application of $\hat{L}_z$, we find that Eq. (5.81) is equivalent to the following expression:

$$\langle \phi|\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial \phi}\langle \phi|. \tag{5.83}$$

Similarly, $\hat{L}_x$ and $\hat{L}_y$ can be shown to be

$$\begin{aligned}\langle \theta, \phi|\hat{L}_x &= \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\langle \theta, \phi| \\ &= i\hbar\left(\sin\phi\frac{\partial}{\partial \theta} + \cot\theta\cos\phi\frac{\partial}{\partial \phi}\right)\langle \theta, \phi|, \end{aligned} \tag{5.84}$$

$$\begin{aligned}\langle \theta, \phi|\hat{L}_y &= \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\langle \theta, \phi| \\ &= i\hbar\left(-\cos\phi\frac{\partial}{\partial \theta} + \cot\theta\sin\phi\frac{\partial}{\partial \phi}\right)\langle \theta, \phi|, \end{aligned} \tag{5.85}$$

where $\langle \theta, \phi| = \langle \theta| \otimes \langle \phi|$ and the fact that $\hat{L}_x$ and $\hat{L}_y$ do not affect $\langle r|$ has been used. Summing the squares of the above two operators, we find that

$$\begin{aligned}\langle \theta, \phi|(\hat{L}_x^2 + \hat{L}_y^2) &= -\hbar^2\left\{\left(\sin\phi\frac{\partial}{\partial \theta} + \cot\theta\cos\phi\frac{\partial}{\partial \phi}\right)^2\right. \\ &\qquad \left. + \left(-\cos\phi\frac{\partial}{\partial \theta} + \cot\theta\sin\phi\frac{\partial}{\partial \phi}\right)^2\right\}\langle \theta, \phi| \\ &= -\hbar^2\left(\frac{\partial^2}{\partial \theta^2} + \cot\theta\frac{\partial}{\partial \theta} + \cot^2\theta\frac{\partial^2}{\partial \phi^2}\right)\langle \theta, \phi|. \end{aligned} \tag{5.86}$$

Summing this with the square of $\hat{L}_z$, we find that

$$\begin{aligned}\langle \theta, \phi|\hat{L}^2 &= \langle \mathbf{r}|(\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) \\ &= -\hbar^2\left(\frac{\partial^2}{\partial \theta^2} + \cot\theta\frac{\partial}{\partial \theta} + \frac{\cos^2\theta + \sin^2\theta}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right)\langle \theta, \phi| \\ &= -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\sin\theta\frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right)\langle \theta, \phi|. \end{aligned} \tag{5.87}$$

Now let us consider application of $\hat{L}^2$ to an arbitrary quantum state $|\psi\rangle$ as follows:

$$\langle\theta,\phi|\hat{L}^2|\psi\rangle = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\langle\theta,\phi|\psi\rangle. \quad (5.88)$$

Note that this is the same as that representing the rotational kinetic energy except for the factor of $1/(2I)$. Therefore, $Y_J^m(\theta,\phi)$ is an eigenfunction of the above differential equation as well. Thus, the spherical harmonics are eigenfunctions of squared angular momentum operator as summarized below.

Rotational Eigenstates and Eigenvalues

Let us define $|J,m\rangle$ such that

$$Y_J^m(\theta,\phi) = \langle\theta,\phi|J,m\rangle. \quad (5.89)$$

Then, Eqs. (5.44) and (5.45) imply that

$$\hat{L}^2|J,m\rangle = \hbar^2 J(J+1)|J.m\rangle, \quad (5.90)$$

$$\hat{L}_z|J,m\rangle = \hbar m|J,m\rangle, \quad (5.91)$$

where $J = 0, 1, 2, \cdots$ and m are integers such that $|m| \leq J$. Note that the reason why $|J,m\rangle$ can be a simultaneous eigenstate of $\hat{L}^2$ and $\hat{L}_z$ is because the two commute with each other.

So far, we have considered rotation of a particle around origin. In fact, the same approach can be used to describe the rotation of a diatomic molecule around its center of mass. For this, let us consider the Hamiltonian operator for the two particle system, Eq. (4.83), in the absence of an external potential and removing the kinetic energy term for the center of mass. Thus, let us consider the following Hamiltonian operator:

$$\hat{H}_{rel} = \frac{\hat{\mathbf{p}}^2}{2\mu} + V_{rel}(\hat{r}), \quad (5.92)$$

where $\mu = m_1m_2/(m_1+m_2)$ is the reduced mass and the fact that the potential energy is a function of r only has been used. Applying this operator on the position bra $\langle\mathbf{r}| = \langle r,\theta,\phi|$ on the lefthand side, we find that

$$\langle r, \theta, \phi | \hat{H}_{rel} = \left(-\frac{\hbar^2}{2\mu} \nabla^2 + V_{rel}(r) \right) \langle r, \theta, \phi | .$$
$$= \left(-\frac{\hbar^2}{2\mu} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + V_{rel}(r) \right) \langle r, \theta, \phi |$$
$$-\frac{\hbar^2}{2\mu r^2} \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right) \langle r, \theta, \phi | . \quad (5.93)$$

In the second equality of the above equation, the first component involving derivatives of r represents vibration motion along the internuclear direction, whereas the second part represents a rotational motion. Note that this part is the same as the rotational Hamiltonian for a particle with effective mass μ. Thus, all the results provided so far for three dimensional rotation of a particle around origin can also be used to describe the quantum states representing the rotation of a diatomic molecule around its center of mass given that the following expression is used for the moment of inertia:

$$I = \mu r^2. \quad (5.94)$$

5.4 Spectroscopy of Rotational Transitions for Diatomic Molecules

We will consider three major transitions involving rotational motions of diatomic molecules. The first is pure rotational transition normally known as microwave spectroscopy. The second is rotational Raman spectroscopy. Finally, we will consider ro-vibrational transitions, where rotational transitions accompany vibrational transitions.

5.4.1 Microwave Spectroscopy

Microwave spectroscopy in general refers to the detection of transitions of rotational states due to linear interaction of the molecular dipole with the electric field component of light. The reason why this is called "microwave" is because the energy level spacings involved are typically in the microwave region. The transition in rotational states occurs because the dipole operator, if not zero, does not commute with the rotational Hamiltonian. Selection rules for this can be understood by considering how different rotational states are coupled by the dipole operator.

Selection Rules for Microwave Spectroscopy of Diatomic Molecules

- If a molecule does not have a permanent dipole, light cannot distinguish different rotational state at the level of the first order interaction. Thus, an important gross selection rule for microwave spectroscopy is that *the molecule has to be polar to be microwave active*.
- The rotational property of the permanent dipole moment, which is proportional to the internuclear distance vector, has the same symmetry property as a three dimensional position vector. Employing the properties of spherical harmonics, it is possible to show that such dipole operator can couple only neighboring rotational quantum numbers. In other words, the following selection rule applies for the microwave spectroscopy of diatomic molecules:

$$\Delta J = \pm 1. \tag{5.95}$$

Microwave spectroscopy is commonly described in terms of rotational constant B defined by the following relationship:

$$E_J = \frac{\hbar^2}{2I} J(J+1) = BJ(J+1), \tag{5.96}$$

where the second equality serves as the definition of B. Typically, the rotational energy is reported in the unit of wavenumber (cm^{-1}) and the following rotational term is often used:

$$G(J) = \frac{E_J}{hc} = \frac{\hbar^2}{2Ihc} J(J+1) = \tilde{B} J(J+1). \tag{5.97}$$

The microwave spectroscopy is in general absorption spectroscopy. Thus, the transition involved is $J \to J+1$, for which the energy difference is given by

$$\Delta E = B(J+1)(J+2) - BJ(J+1) = 2B(J+1). \tag{5.98}$$

The corresponding wavenumber is given by

$$\Delta \tilde{\nu} = \frac{\Delta E}{hc} = 2\tilde{B}(J+1). \tag{5.99}$$

As Eq. (5.98) or (5.99) shows, the rotational transition energy or wavenumber increases linearly with the initial total angular momentum quantum number J. This is in contrast to the vibrational transition of a harmonic oscillator where there is

only one transition energy, within the harmonic oscillator approximation. For this reason, the microwave spectroscopy appears as a packet of transition lines rather than a single or few transitions.

Since the interaction strength between the dipole and the electric field does not change significantly with the rotational state of the molecule, the intensity of each rotational transition is proportional to the relative population of molecule in the specific initial rotational state with quantum number J. For a given rotational state with J, there are $2J + 1$ degenerate states because any of $m_J = -J, \cdots, J$ is possible. In other words, a given angular momentum quantum number J has $2J + 1$ degeneracy. Therefore, the probability of having the molecule in the J state is proportional to this degeneracy multiplied by the Boltzmann factor as follows:

$$p_J = \frac{(2J+1)\exp\left\{-\frac{BJ(J+1)}{k_B T}\right\}}{\sum_{J=0}^{\infty}(2J+1)\exp\left\{-\frac{BJ(J+1)}{k_B T}\right\}}. \tag{5.100}$$

5.4.2 *Rotational Raman Spectroscopy*

Rotational Raman spectroscopy probes transition of rotational states due to the interaction of the polarizability of a molecule with light, which is second order with respect to the electric field amplitude of the light. Selection rules for the rotational Raman spectroscopy can be understood considering this aspect.

Selection Rules for Rotational Raman Spectroscopy

- Any molecule that changes its polarizability with rotation is active in the rotational Raman spectroscopy. This means that the molecule should have anisotropic polarizability, which is always the case for diatomic molecules.
- Since polarizability is independent of the sign of rotation, it is easy to see that it is an even function of angles and is invariant after rotation by 180° degrees. This symmetry property makes the selection rule for rotational Raman different from the microwave spectroscopy and results in the following selection rule:

$$\Delta J = \pm 2. \tag{5.101}$$

- The positive case is Stokes Raman transition and the negative case is anti-Stokes Raman transition. For the Stokes Raman transition from J to $J+2$, the magnitude of the transition energy (in wave number) is

$$\Delta\tilde{\nu} = \tilde{B}\left\{(J+2)(J+3) - J(J+1)\right\} = 2\tilde{B}(2J+3). \tag{5.102}$$

5.4.3 Ro-Vibrational Transition

For the understanding of ro-vibrational transition, it is necessary to consider the diatomic molecular Hamiltonian given by Eq. (5.92) in more detail. For $|\psi_E\rangle$, an eigenstate of this Hamiltonian with eigenvalue E, applying the Hamiltonian for the relative motion part and then taking inner product with the position bra, we find that

$$\begin{aligned}\langle r,\theta,\phi|\hat{H}_{rel}|\psi_E\rangle &= \left\{\left(-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + V_{rel}(r)\right)\right.\\ &\left.-\frac{\hbar^2}{2\mu r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\right\}\psi_E(r,\theta,\phi)\\ &= E\psi_E(r,\theta,\phi),\end{aligned} \tag{5.103}$$

where $\psi_E(r,\theta,\phi) = \langle r,\theta,\phi|\psi_E\rangle$ and Eq. (5.93) has been used. Let us assume that

$$\psi_E(r,\theta,\phi) = \frac{1}{r}\psi_v(r)Y_{JM}(\theta,\phi). \tag{5.104}$$

Inserting this expression into Eq. (5.103), and factoring out the common function $Y_{JM}(\theta,\phi)$, we find that

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V_J^{eff}(r)\right)\psi_v(r) = E\psi_v(r), \tag{5.105}$$

where

$$V_J^{eff}(r) = V_{rel}(r) + \frac{\hbar^2 J(J+1)}{2\mu r^2}. \tag{5.106}$$

Let r_e be the equilibrium internuclear distance of the diatomic molecule. If the internuclear potential energy is strong enough, the deviation, $s = r - r_e$, is very small compared to r_e. Indeed, this is the case for most diatomic molecules consisting of light atoms. Then, the moment of inertia in this case can be approximated as $I = \mu r^2 \approx \mu r_e^2$ in the above equation and

$$V_J^{eff}(r) \approx V_{rel}(r) + B_e J(J+1), \tag{5.107}$$

where $B_e = \hbar^2/(2I_e) = \hbar^2/(2\mu r_e^2)$. Let us also assume that $V_{rel}(r)$ can be approximated as a parabolic potential around r_e with curvature $V''_{rel}(r_e) = \mu\omega^2$. Thus $V_{rel}(r) \approx V_{rel}(r_e) + \mu\omega_e^2(r-r_e)^2/2$. Then, Eq. (5.108) can be approximated as

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{ds^2}+\frac{1}{2}\mu\omega_e^2 s^2+V_{rel}(r_e)+B_e J(J+1)\right)\psi_v(r_e+s)=E\psi_v(r_e+s), \tag{5.108}$$

where we have introduced a new coordinate $s = r - r_e$.

Equation (5.108) is the same as the Schrödinger equation for the harmonic oscillator except for the constant terms and the addition of rotational energy, which is independent of r. Therefore, the corresponding eigenfunction is the same as that for the harmonic oscillator as follows:

$$\psi_v(r_e+s)=N_v e^{-\gamma s^2/2} H_v(\sqrt{\gamma}s), \tag{5.109}$$

where $\gamma = \sqrt{\mu\omega_e/\hbar}$, N_v is the normalization constant, and $H_v(\sqrt{\gamma}s)$ is the Hermite polynomial. On the other hand, the eigenvalue is

$$E_{v,J}=\hbar\omega_e\left(v+\frac{1}{2}\right)+B_e J(J+1)+V_{rel}(r_e). \tag{5.110}$$

The above expression shows that the eigenstate of a diatomic molecule, in its simplest approximation of $I \approx I_e$, can be viewed as the direct product of the vibrational and rotational states, namely, $|v\rangle \otimes |J, m\rangle$. Now, note that the dipole vector is given by

$$\mathbf{D}=q\mathbf{r}=q(r_e+s)\left(\mathbf{e_x}\sin\theta\cos\phi+\mathbf{e}_y\sin\theta\sin\phi+\mathbf{e}_z\cos\theta\right), \tag{5.111}$$

where q is the partial nuclear charge of the diatomic molecule and $\mathbf{e}_x$, $\mathbf{e}_y$, and $\mathbf{e}_z$ are unit vectors along x, y, and z coordinates. Thus, the measurement of dipole moment in fact involves measuring both the internuclear distance and angle of the molecule.

If the energy of light is small enough not to excite any vibrational motion, it is possible that only rotational states are altered. This is the case of the microwave spectroscopy. However, for the case of IR spectroscopy that involves transition of vibrational energies, it is inevitable that rotational states change as well because the energy for rotational energy is readily available and there is nothing that prevents the rotational transition from accompanying the vibrational transition. *The selection rule governing the rotational transition in this case is the same as the microwave spectroscopy because the same dipole operator is involved.* Since wavenumber is used for the description of these ro-vibrational transitions, it is convenient to introduce the corresponding ro-vibrational term as follows:

$$G(v,J)=\frac{E_{v,J}}{hc}=\tilde{\nu}_e(v+\frac{1}{2})+\tilde{B}_e J(J+1). \tag{5.112}$$

Selection Rules for RO-Vibrational Transitions and P, Q, and R Branches

- Due to the availability of rotational transition during vibrational transition as noted above, in any IR spectroscopy, not only the vibrational quantum number changes according to $\Delta v = 1$ but the rotational quantum number J also changes in general. For the case of most diatomic molecules,[1] $\Delta J = \pm 1$.
- The transitions corresponding to $\Delta J = -1$ form the P-branch and have the following wavenumbers:

$$\tilde{\nu}_P(J) = \tilde{\nu}_e + \tilde{B}_e(J-1)J - \tilde{B}_e J(J+1) = \tilde{\nu}_e - 2\tilde{B}_e J. \tag{5.113}$$

- The transitions corresponding to $\Delta J = 1$ form the R-branch and have the following wavenumbers:

$$\tilde{\nu}_R(J) = \tilde{\nu}_e + \tilde{B}_e(J+1)(J+2) - \tilde{B}_e J(J+1) = \tilde{\nu}_e + 2\tilde{B}_e(J+1). \tag{5.114}$$

- The transitions corresponding to $\Delta J = 0$, which is normally forbidden, form the Q-branch and the corresponding wavenumber is $\tilde{\nu}_e$.

[1] There are few exceptions for this such as the molecule NO, for which $\Delta J = 0$ is also possible. Such exception occurs due to the special nature of the electronic states that contributes to the angular momentum.

The above selection rules are based on the approximation that the vibrational and rotational motion are decoupled from each other and that there are no centrifugal distortion. Complications that arise when these are included are described in the next subsection.

5.4.4 *Centrifugal Correction and Ro-Vibrational Coupling*

In actual diatomic molecules, corrections need to be made for the distortion of bond distance due to centrifugal distortion and the coupling between vibration and rotation. As long as such effects are small, they can be added as small corrections. For this, let us expand $V_{rel}(r)$ and $\hbar^2 J(J+1)/r^2$ in Eq. (5.106) around r_e as follows:

$$V_{rel}(r_e + s) \approx V_{rel}(r_e) + \frac{1}{2}\mu\omega^2 s^2 - \frac{1}{3!}\kappa s^3, \tag{5.115}$$

$$\begin{aligned}\frac{\hbar^2 J(J+1)}{2\mu(r_e+s)^2} &= \frac{\hbar^2 J(J+1)}{2\mu r_e^2}\left(1+\frac{s}{r_e}\right)^{-2} \\ &\approx \frac{\hbar^2 J(J+1)}{2\mu r_e^2}\left(1 - 2\frac{s}{r_e} + 3\frac{s^2}{r_e^2}\right).\end{aligned} \tag{5.116}$$

From these approximations, we find the following expressions for the first and the second derivatives of $V_J^{eff}(r)$:

$$\frac{d}{ds}V_J^{eff}(r) \approx \mu\omega_e^2 s - \frac{1}{2}\kappa s^2 - \frac{\hbar^2 J(J+1)}{\mu r_e^3} + \frac{3\hbar^2 J(J+1)}{\mu r_e^4}s, \tag{5.117}$$

$$\frac{d^2}{ds^2}V_J^{eff}(r) \approx \mu\omega_e^2 - \kappa s + \frac{3\hbar^2 J(J+1)}{\mu r_e^4}. \tag{5.118}$$

In Eq. (5.117), let us consider only the constant term and the most dominant linear term, $\mu\omega_e^2 s$, in order to find a new minimum of the potential energy, s_e. That is, for s_e, the following relation is assumed:

$$\mu\omega_e^2 s_e - \frac{\hbar^2 J(J+1)}{\mu r_e^3} \approx 0. \tag{5.119}$$

Solving this equation, we find that

$$s_e \approx \frac{\hbar^2 J(J+1)}{\mu^2\omega_e^2 r_e^3}. \tag{5.120}$$

This can be understood as the shift of the potential minimum due to the centrifugal force. Inserting this value into Eq. (5.118),

$$\begin{aligned}\left.\frac{d^2}{ds^2}V_J^{eff}(r_e+s)\right|_{s=s_e} &\approx \mu\omega_e^2 - \frac{\kappa\hbar^2 J(J+1)}{\mu^2\omega_e^2 r_e^3} + \frac{3\hbar^2 J(J+1)}{\mu r_e^4} \\ &\equiv \mu\omega_J^2.\end{aligned} \tag{5.121}$$

where

$$\omega_J = \omega_e\left(1 - \frac{\kappa\hbar^2 J(J+1)}{\mu^3\omega_e^4 r_e^3} + \frac{3\hbar^2 J(J+1)}{\mu^2\omega_e^2 r_e^4}\right)^{1/2}. \tag{5.122}$$

Then, making quadratic expansion of V_J^{eff} around $r_e + s_e$, we find that

$$\begin{aligned} V_J^{eff}(r_e + s) &\approx V_{rel}(r_e) + \frac{1}{2}\mu\omega_J^2(s - s_e)^2 - \frac{\mu\omega_J^2}{2}s_e^2 + \frac{\hbar^2 J(J+1)}{2I_e} \\ &= V_0 + \frac{1}{2}\mu\omega_J^2(s - s_e)^2 + \frac{\hbar^2}{2I_e}J(J+1) - \frac{\hbar^4}{2\omega_e^2 I_e^3}J^2(J+1)^2. \end{aligned} \tag{5.123}$$

Now inserting this new form of effective potential into Eq. (5.108), one can find the following expression for the eigenvalue:

$$E_{v,J} = V_0 + \hbar\omega_J(v + \frac{1}{2}) + \frac{\hbar^2}{2I_e}J(J+1) - \frac{\hbar^4}{2\omega_e^2 I_e^3}J^2(J+1)^2, \tag{5.124}$$

where ω_J is defined by Eq. (5.122) and the last term corresponds to the centrifugal distortion energy. Further approximation of Eq. (5.122) can be made. Let us introduce

$$\alpha_e = \frac{1}{2}\left(\frac{\kappa\hbar^3}{\mu^3\omega_e^4 r_e^3} - \frac{3\hbar^3}{\mu^2\omega_e^2 r_e^4}\right). \tag{5.125}$$

In general, $\alpha_e << \hbar$. Thus,

$$\omega_J = \omega_e\left(1 - 2\alpha_e\frac{J(J+1)}{\hbar}\right)^{1/2} \approx \omega - \frac{\alpha_e\omega_e}{\hbar}J(J+1). \tag{5.126}$$

Inserting this into Eq. (5.124) and also introducing centrifugal distortion constant

$$D_e = \frac{\hbar^4}{2\omega_e^2 I_e^3}, \tag{5.127}$$

we find that

$$\begin{aligned} E_{v,J} &\approx V_0 + \hbar\left(\omega_e - \frac{\alpha_e}{\hbar}J(J+1)\right)(v + \frac{1}{2}) + B_e J(J+1) - D_e J^2(J+1)^2 \\ &= V_0 + \hbar\omega_e(v + \frac{1}{2}) + B_e J(J+1) + \delta E_{rot}^{v,J}, \end{aligned} \tag{5.128}$$

where

$$\delta E_{rot}^{v,J} = -\alpha_e(v + \frac{1}{2})J(J+1) - D_e J^2(J+1)^2. \tag{5.129}$$

The first term in the above correction term comes from the coupling between the vibration and rotation and the second term comes from the centrifugal distortion. Note that both terms reduce the rotational energy level spacings because they effectively increase the moment of inertia.

Let us first consider the case of rotational states for vibrational ground state, $v = 0$. The rotational energy level (without including the constant term) is given by

$$E_J = B_0 J(J+1) - D_e J^2 (J+1)^2, \tag{5.130}$$

where

$$B_0 = B_e - \frac{\alpha_e}{2}. \tag{5.131}$$

The corresponding rotational energy term is as follows:

$$G(J) = \tilde{B}_0 J(J+1) - \tilde{D}_e J^2 (J+1)^2, \tag{5.132}$$

where $\tilde{B}_0 = B_0/(hc)$ and $\tilde{D}_e = D_e/(hc)$. With this expression, the correction for the rotational transition wavenumber, for the case of $J \to J+1$, can be shown to be

$$\begin{aligned}\Delta\tilde{\nu}(J \to J+1) &= \tilde{B}_0(J+1)(J+2) - \tilde{D}_e(J+1)^2(J+2)^2 \\ &\quad -\tilde{B}_0 J(J+1) + \tilde{D}_e J^2(J+1)^2 \\ &= 2\tilde{B}_0(J+1) - \tilde{D}_e(J+1)^2(4J+4) \\ &= 2\tilde{B}_0(J+1) - 4\tilde{D}_e(J+1)^3. \end{aligned} \tag{5.133}$$

Note that the reduction of the level spacing due to the centrifugal distortion depends on the third order of $(J+1)$.

Next, let us consider the effects of the coupling of rotational and vibrational states, but without including the effects of the centrifugal distortion. The corresponding term for the state in this case is given by

$$G(v, J) = \tilde{\nu}_e(v + \frac{1}{2}) + \tilde{B}_v J(J+1), \tag{5.134}$$

where

$$\tilde{B}_v = \tilde{B}_e - \tilde{\alpha}_e(v + \frac{1}{2}), \tag{5.135}$$

with $\tilde{\alpha}_e = \alpha_e/(hc)$. The above expression implies that the rotational constant decreases as the vibrational quantum number increases. This is because larger vibrational quantum number results in larger moment of inertia. Note that the rotational constant is inversely proportional to the moment of inertia. Given the

above term, the P-branch, assuming that the vibrational transition is $\upsilon = 0 \rightarrow 1$, now has the following expression:

$$\begin{aligned}\tilde{\nu}_P(J) &= \tilde{\nu}_e + \tilde{B}_1 J(J-1) - \tilde{B}_0 J(J+1) \\ &= \tilde{\nu}_e + (\tilde{B}_1 - \tilde{B}_0)J^2 - (\tilde{B}_1 + \tilde{B}_0)J \\ &= \tilde{\nu}_e - \tilde{\alpha}_e J^2 - 2(\tilde{B}_e - \tilde{\alpha}_e)J. \end{aligned} \tag{5.136}$$

This P-branch has lower energy than the original pure vibrational transition, with the red shift increasing (becoming more negative) as J increases. The level spacing of this P-branch between consecutive values of J increases as J increases. On the other hand, the R-branch has the following expression:

$$\begin{aligned}\tilde{\nu}_R(J) &= \tilde{\nu}_e + \tilde{B}_1 (J+1)(J+2) - \tilde{B}_0 J(J+1) \\ &= \tilde{\nu}_e + (\tilde{B}_1 - \tilde{B}_0)J^2 + (3\tilde{B}_1 - \tilde{B}_0)J + 2\tilde{B}_1 \\ &= \tilde{\nu}_e - \tilde{\alpha}_e J^2 + (2\tilde{B}_e - 4\tilde{\alpha}_e)J + 2\tilde{B}_e - 3\tilde{\alpha}_e. \end{aligned} \tag{5.137}$$

This R-branch has higher energy than the original vibrational transition ($J = 0$), and shows blue shift (at least for small values of J) as J increases. However, the difference of transition energies between consecutive values of J within this R-branch decreases as J increases. For sufficiently large value of J, the above expression predicts that $\tilde{\nu}_R(J)$ decreases as J increases. This is called "reversal of R-head" [31].

5.5 Summary and Questions

Eigenvalues and eigenfunctions of two dimensional rotation (or rotation around the z-axis) are given by Eqs. (5.24) and (5.26), respectively. For three dimensional rotation, separation of variables in spherical coordinate system leads to an equation for the axial angle θ, the solution of which is related to associated Legendre functions provided in Table 5.1. Combination of these with eigenfunctions for the two-dimensional rotation results in spherical harmonics defined by Eq. (5.42) as eigenfunctions for the three dimensional rotation with eigenvalues given by Eq. (5.43).

Alternatively, three dimensional rotational Hamiltonian can be expressed in terms of the angular momentum square operator as shown in Eq. (5.54). Spherical harmonics are simultaneous eigenfunctions of the angular momentum square operator and the z-component of the angular momentum operator, and serve as a complete basis for describing any three dimensional rotational motion. This is also related with the fact that three different cartesian components of the angular momentum operators do not commute with each other, as shown in Eqs. (5.58)–(5.60), making it impossible to specify more than one of them.

The rotational spectroscopy of diatomic molecules, which are approximated as rigid rotors, can be fully described in terms of the interaction of dipole operator or polarization operator associated with the rotation and electric fields. Microwave spectroscopy involves interaction with the dipole operator, for which the selection rule is given by Eq. (5.95). Rotational Raman spectroscopy involves interaction with the polarization operator, for which the selection rule is given by Eq. (5.101). It is also important to note that change of rotational states accompany vibrational transition in general, typically resulting in two major branches called P and R, as expressed respectively by Eqs. (5.136) and (5.137). It has long been an experimental convention to express all of rotational transition energies in the unit of wavenumber, cm^{-1}, for which rotational constants serve as a natural unit of energy.

For flexible molecules or for molecules in highly excited rotational states, the assumption of rigid rotor breaks down. Inclusion of the effect of centrifugal distortion is possible by adding corrections for each rotational level as long as its effect remains small. Combining this with the change of moment of inertia associated with different vibrational level, it is possible to obtain an approximate expression for the ro-vibrational level as shown in Eq. (5.128). This expression provides more satisfactory description of ro-vibrational transitions of many diatomic molecules.

Questions

- What are physical origins for the quantization of rotational energies?
- Why are quantum states for three dimensional rotation appear to be much more complicated than those for two dimensional rotation?
- What is the degeneracy for a two dimensional rotational quantum number m?
- What is the degeneracy for a three dimensional rotational quantum number J?
- What is the physical meaning of the moment of inertia?
- Why is it impossible to determine eigenstates of more than one components of the angular momentum vector operator?
- Is angular momentum a conserved quantity for a diatomic molecule in space free of any external potentials?
- Can a molecule with zero permanent dipole moment still be active in rotational Raman spectroscopy?
- Why do multiple transition lines exist in the rotational spectroscopy even for the simplest case of a diatomic molecule?
- Why does centrifugal distortion tend to reduce rotational level spacings as the rotational quantum number increases?

Appendix: Associated Legendre Equations and Their Solutions

Let us first consider the case where $m = 0$ in Eq. (5.37) as follows:

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\Theta(\theta)\right) + \beta\Theta(\theta) = 0, \tag{5.138}$$

which is called Legendre equation (with appropriate choice of β as will be clear below). Let us introduce $x = \cos\theta$ and $\Theta(\theta) = f(x)$. Since $dx = -\sin\theta d\theta$, Eq. (5.138) can be expressed as

$$\frac{d}{dx}\left((1-x^2)\frac{d}{dx}f(x)\right) + \beta f(x) = 0. \tag{5.139}$$

Let us assume that $f(x)$ can be expressed as the following power series:

$$f(x) = \sum_{k=0}^{\infty} C_k x^{k+p}, \tag{5.140}$$

where p is the order of the first term and has to be determined by solving the equation. Taking the derivative of $f(x)$ and multiplying with $(1 - x^2)$, and then taking derivative again, we obtain

$$\begin{aligned}\frac{d}{dx}\left((1-x^2)\frac{d}{dx}f(x)\right) &= \sum_{k=0}^{\infty} C_k\Big\{(k+p)(k+p-1)x^{k+p-2}\\ &\qquad -(k+p)(k+p+1)x^{k+p}\Big\}\\ &= C_0 p(p-1)x^{p-2} + C_1(p+1)px^{p-1}\\ &\quad + \sum_{k=0}^{\infty}\{C_{k+2}(k+p+2)(k+p+1)\\ &\qquad -C_k(k+p)(k+p+1)\}\, x^{k+p}.\end{aligned} \tag{5.141}$$

Combining this with Eq. (5.140) in Eq. (5.139), we obtain

$$\begin{aligned}&C_0 p(p-1)x^{p-2} + C_1(p+1)px^{p-1}\\ &+\sum_{k=0}^{\infty}\{C_{k+2}(k+p+2)(k+p+1) - C_k(k+p)(k+p+1) + C_k\beta\}\, x^{k+p} = 0.\end{aligned} \tag{5.142}$$

The first two terms are zero if $p = 0$, for which one can assume either $C_0 = 0$ or $C_1 = 0$. The choice of $p = 1$ with $C_1 = 0$ or $p = -1$ with $C_0 = 0$ is equivalent to one of these cases. Thus, without losing any generality, we can assume that $p = 0$. For Eq. (5.142) to be satisfied, each coefficient for x^k should be zero. This means that

$$C_{k+2} = \frac{k(k+1) - \beta}{(k+2)(k+1)} C_k. \tag{5.143}$$

Now let us consider the large k limit, for which $C_{k+2} \sim C_k$. This means that, as x approaches ± 1, $f(x) \sim 1/(1-x^2)$ if $C_1 = 0$ and $f(x) \sim x/(1-x^2)$ if $C_0 = 0$. The resulting wavefunction in this case is not normalizable. Therefore, for the solution to be physically acceptable, the series has to terminate at finite order of x. Thus, let us assume that the series terminate at x^J. This is possible if

$$\beta = J(J+1), \tag{5.144}$$

where $J = 0, 1, \cdots$. The resulting solution of Eq. (5.139) for each case of J is called Legendre polynomial of order J and is denoted as $P_J(x)$.

Let us now consider the case where $m \neq 0$ in Eq. (5.37) for β given by Eq. (5.144). Employing the same $x = \cos\theta$ as variable, it can be expressed as

$$\frac{d}{dx}\left((1-x^2)\frac{d}{dx}f(x)\right) + \left(J(J+1) - \frac{m^2}{(1-x^2)}\right) f(x) = 0. \tag{5.145}$$

Note that the additional term $-m^2/(1-x^2)$ multiplied to $f(x)$ becomes singular for $x = \pm 1$, for which, $\theta = 0, \pi$. This singular term has to be taken care of before assuming power series for the solution. This can be achieved by introducing another function $g(x)$ such that

$$f(x) = (1-x^2)^{|m|/2} g(x). \tag{5.146}$$

Why the above form removes the singularity can be understood considering the leading contribution from the second derivative of $f(x)$, as detailed below. Taking the derivative of Eq. (5.146) with respect to x and multiplying it with $(1-x^2)$, we obtain,

$$(1-x^2)\frac{d}{dx}f(x) = -|m|x(1-x^2)^{|m|/2}g(x) + (1-x^2)^{|m|/2+1}\frac{d}{dx}g(x). \tag{5.147}$$

Taking derivative of the above equation one more time with respect to x, we obtain

$$\begin{aligned}\frac{d}{dx}(1-x^2)\frac{d}{dx}f(x) &= -|m|(1-x^2)^{|m|/2}g(x) + m^2x^2(1-x^2)^{|m|/2-1}g(x)\\ &\quad -|m|x(1-x^2)^{|m|/2}\frac{d}{dx}g(x) - (|m|+2)x(1-x^2)^{|m|/2}\frac{d}{dx}g(x)\\ &\quad +(1-x^2)^{|m|/2+1}\frac{d^2}{dx^2}g(x)\\ &= -(|m|+m^2)(1-x^2)^{|m|/2}g(x) + m^2(1-x^2)^{|m|/2-1}g(x)\\ &\quad -(2|m|+2)x(1-x^2)^{|m|/2}\frac{d}{dx}g(x)\\ &\quad +(1-x^2)^{|m|/2+1}\frac{d^2}{dx^2}g(x). \end{aligned} \tag{5.148}$$

Using this expression and Eq. (5.146) in Eq. (5.149) and then rearranging terms, we find that

$$\begin{aligned}(1-x^2)^{|m|/2}\left\{\frac{d}{dx}\left((1-x^2)\frac{d}{dx}g(x)\right) - 2|m|x\frac{d}{dx}g(x)\right.\\ \left. + \Big(J(J+1) - (m^2+|m|)\Big)g(x)\right\} = 0. \end{aligned} \tag{5.149}$$

Since this has to be satisfied for any value of x, $(1-x^2)^{|m|/2}$ can be factored out. In addition, using the fact that $J(J+1) - (m^2+|m|) = (J-|m|)(J+|m|+1)$, we obtain

$$\frac{d}{dx}\left((1-x^2)\frac{d}{dx}g(x)\right) - 2|m|x\frac{d}{dx}g(x) + (J-|m|)(J+|m|+1)g(x) = 0. \tag{5.150}$$

Note that the above equation is similar to Eq. (5.139) except for additional first derivative term. In fact, $g(x)$ can be related to $P_J(x)$ through derivatives as shown below.

Let us consider the Legendre polynomial $P_J(x)$, which is the solution of the following differential equation:

$$(1-x^2)\frac{d^2}{dx^2}P_J(x) - 2x\frac{d}{dx}P_J(x) + J(J+1)\frac{d}{dx}P_J(x) = 0, \tag{5.151}$$

where we have separated out the first and second derivative terms. Taking the derivative of this equation with respect to x, we obtain

$$(1-x^2)\frac{d^3}{dx^3}P_J(x) - 4x\frac{d^2}{dx^2}P_J(x) + (J(J+1)-2)\frac{d}{dx}P_J(x) = 0. \tag{5.152}$$

Taking the derivative of the above equation once again, we also obtain

$$(1-x^2)\frac{d^4}{dx^4}P_J(x) - 6x\frac{d^3}{dx^3}P_J(x) + (J(J+1)-2-4)\,\frac{d^2}{dx^2}P_J(x) = 0. \tag{5.153}$$

Inspection of the above two equations shows that the following general relation, which can be proved by taking derivatives of Eq. (5.153) for $|m|$ times, is satisfied.

$$\begin{aligned}
&(1-x^2)\frac{d^{|m|+2}}{dx^{|m|+2}}P_J(x) - 2(|m|+1)x\frac{d^{|m|+1}}{dx^{|m|+1}}P_J(x) \\
&\quad +(J(J+1)-|m|-m^2)\frac{d^{|m|}}{dx^{|m|}}P_J(x) \\
&= \frac{d}{dx}\left((1-x^2)\frac{d}{dx}\left(\frac{d^{|m|}}{dx^{|m|}}P_J(x)\right)\right) - 2|m|x\frac{d}{dx}\left(\frac{d^{|m|}}{dx^{|m|}}P_J(x)\right) \\
&\quad +(J-|m|)(J+|m|+1)\left(\frac{d^{|m|}}{dx^{|m|}}P_J(x)\right) = 0.
\end{aligned} \tag{5.154}$$

This last equation is exactly the same form as Eq. (5.150). Thus, we find the following solution:

$$g(x) = \frac{d^{|m|}}{dx^{|m|}}P_J(x). \tag{5.155}$$

Since $P_J(x)$ is a polynomial of order J, the following condition should hold

$$|m| \le J. \tag{5.156}$$

Combining this with Eq. (5.146), we obtain the following definition of associated Legendre function:

$$P_J^{|m|}(x) = (1-x^2)^{|m|/2}\frac{d^{|m|}}{dx^{|m|}}P_J(x). \tag{5.157}$$

Whether there are other physically acceptable solutions of the associated Legendre equation that can be defined for $-1 \le x \le 1$ is a rather subtle issue, but can be ruled out after more careful consideration [32].

Exercise Problems with Solutions

5.1 Prove that $Y_2^1(\theta,\phi)$ in Table 5.2 satisfies Eq. (5.33) and determine the corresponding eigenvalue E for this function.

Solution 5.1 $Y_2^1(\theta,\phi) = N \sin\theta\cos\theta e^{i\phi}$, where $N = -(15/8\pi)^{1/2}$. Application of the differentiation with respect to θ constituting $\hat{L}^2$ to $Y_2^1(\theta,\phi)$ is thus proportional to

$$\begin{aligned}
&\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\sin\theta\cos\theta e^{i\phi} \\
&= \frac{1}{\sin\theta}\left(\sin\theta(\cos^2\theta - \sin^2\theta)e^{i\phi}\right) \\
&= \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\cos(2\theta)e^{i\phi}\right) \\
&= \frac{1}{\sin\theta}\left(\cos\theta\cos(2\theta) - 2\sin\theta\sin(2\theta)\right)e^{i\phi} \\
&= \frac{1}{\sin\theta}\left(\cos\theta(\cos^2\theta - \sin^2\theta) - 4\sin^2\theta\cos\theta\right)e^{i\phi} \\
&= \left(\frac{1}{\sin\theta}\cos\theta - 6\sin\theta\cos\theta\right)e^{i\phi}.
\end{aligned}$$

On the other hand,

$$\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\sin\theta\cos\theta e^{i\phi} = -\frac{1}{\sin\theta}\cos\theta e^{i\phi}.$$

Therefore,

$$\begin{aligned}
&-\frac{\hbar^2}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)Y_2^1(\theta,\phi) \\
&= -\frac{\hbar^2}{2I}\left(\frac{1}{\sin^2\theta} - 6 - \frac{1}{\sin^2\theta}\right)Y_2^1(\theta,\phi) = \frac{6\hbar^2}{2I}Y_2^1(\theta,\phi).
\end{aligned}$$

5.2 Prove that $[\hat{L}_y, \hat{L}_z] = i\hbar L_x$ in a way similar to Eq. (5.61).

Solution 5.2 Employing the definitions of $\hat{L}_y$ and $\hat{L}_z$,

$$\begin{aligned}
[\hat{L}_y, \hat{L}_z] &= [\hat{z}\hat{p}_x - \hat{x}\hat{p}_z, \hat{x}\hat{p}_y - \hat{y}\hat{p}_x] \\
&= [\hat{z}\hat{p}_x, \hat{x}\hat{p}_y] - [\hat{x}\hat{p}_z, \hat{x}\hat{p}_y] - [\hat{z}\hat{p}_x, \hat{y}\hat{p}_x] + [\hat{x}\hat{p}_z, \hat{y}\hat{p}_x] \\
&= \hat{z}[\hat{p}_x, \hat{x}]\hat{p}_y + \hat{y}[\hat{x}, \hat{p}_x]\hat{p}_z \\
&= -i\hbar\hat{z}\hat{p}_y + i\hbar\hat{y}\hat{p}_z = i\hbar\hat{L}_x.
\end{aligned}$$

5.3 Prove that $[\hat{L}^2, \hat{L}_x] = 0$ in a way similar to Eq. (5.62).

Solution 5.3 Employing the fact that $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$,

$$
\begin{aligned}
[\hat{L}^2, \hat{L}_x] &= [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x] \\
&= \hat{L}_y[\hat{L}_y, \hat{L}_x] + [\hat{L}_y, \hat{L}_x]\hat{L}_y + \hat{L}_z[\hat{L}_z, \hat{L}_x] + [\hat{L}_z, \hat{L}_x]\hat{L}_z \\
&= \hat{L}_y(-i\hbar\hat{L}_z) + (-i\hbar\hat{L}_z)\hat{L}_y + \hat{L}_z(i\hbar\hat{L}_y) + (i\hbar\hat{L}_y)\hat{L}_z = 0.
\end{aligned}
$$

5.4 Prove that the following wave function is an eigenfunction of $\hat{L}^2$ and find the eigenvalue. Is this also an eigenfunction of $\hat{L}_z$? Provide clear basis for your answer.

$$
\psi(\theta, \phi) = \left(\frac{5}{32\pi}\right)^{1/2} \left(3\cos^2\theta + \sqrt{\frac{3}{2}}\sin^2\theta e^{2i\phi} - 1\right).
$$

Solution 5.4 Let us first consider the following operation:

$$
\begin{aligned}
&\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\left(3\cos^2\theta + \sqrt{\frac{3}{2}}\sin^2\theta e^{2i\phi} - 1\right) \\
&= \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\left(6\cos\theta(-\sin\theta) + \sqrt{\frac{3}{2}}2\sin\theta\cos\theta e^{2i\phi}\right) \\
&= \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\sin(2\theta)\left(-3 + \sqrt{\frac{3}{2}}e^{2i\phi}\right) \\
&= \frac{1}{\sin\theta}(\cos\theta\sin(2\theta) + 2\sin\theta\cos(2\theta))\left(-3 + \sqrt{\frac{3}{2}}e^{2i\phi}\right) \\
&= (4\cos^2\theta - 2\sin^2\theta)\left(-3 + \sqrt{\frac{3}{2}}e^{2i\phi}\right) \\
&= -6(3\cos^2\theta - 1) + \sqrt{\frac{3}{2}}(4 - 6\sin^2\theta)e^{2i\phi}.
\end{aligned}
$$

On the other hand,

$$
\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\left(3\cos^2\theta + \sqrt{\frac{3}{2}}\sin^2\theta e^{2i\phi} - 1\right) = -\sqrt{\frac{3}{2}}4e^{2i\phi}.
$$

Combining the above two results,

$$\hat{L}^2\psi(\theta,\phi) = -\hbar^2\left(\frac{5}{32\pi}\right)^{1/2}\left(-6(3\cos^2\theta - 1) - 6\sqrt{\frac{3}{2}}\sin^2\theta e^{2i\phi}\right)$$
$$= 6\hbar^2\psi(\theta,\phi).$$

Thus, $\psi(\theta,\phi)$ is an eigenfunction of $\hat{L}^2$ with eigenvalue $6\hbar^2$. On the other hand,

$$\hat{L}_z\psi(\theta,\phi) = \left(\frac{5}{32\pi}\right)^{1/2}\frac{\hbar}{i}\frac{\partial}{\partial\phi}\left(3\cos^2\theta + \sqrt{\frac{3}{2}}\sin^2\theta e^{2i\phi} - 1\right)$$
$$= \left(\frac{5}{32\pi}\right)^{1/2}\sqrt{\frac{3}{2}}2\hbar\sin^2\theta e^{2i\phi}.$$

This is not proportional to $\psi(\theta,\phi)$. Therefore, $\psi(\theta,\phi)$ is not an eigenfunction of $\hat{L}_z$.

5.5 Diatomic molecule H_2 and its deuterium isotope D_2 have the same internuclear bond distance 0.748 Å. Calculate the values of rotational constant, $\tilde{B}$, and the three lowest rotational energy levels in the unit of wavenumber cm^{-1}.

Solution 5.5 The rotational constant $\tilde{B}$ is given by the following expressions:

$$\tilde{B} = \frac{\hbar^2}{2Ihc} = \frac{\hbar^2}{2\mu R^2 hc} = \frac{h}{8\pi^2\mu R^2 c},$$

where $R = 0.748$ Å is the internuclear distance and μ is the reduced mass. For H_2, $\mu_{H_2} = m_H/2 = 1.0078 \times 1.6605 \times 10^{-27}/2$ kg $= 8.3673 \times 10^{-25}$ g. For D_2, $\mu_{D_2} = m_D/2 = 2.01410 \times 1.6605 \times 10^{-27}/2$ kg $= 1.6722 \times 10^{-24}$ g. Therefore, $\tilde{B}_{H_2} = 59.79$ cm^{-1} and $\tilde{B}_{D_2} = 29.92$ cm^{-1}. With these values, we obtain the following values for the energies of three lowest rotational energy levels:

	$J = 0$	$J = 1$	$J = 2$
H_2	0	1.196×10^2 cm^{-1}	3.587×10^2 cm^{-1}
D_2	0	5.984×10 cm^{-1}	1.795×10^2 cm^{-1}

5.6 The equilibrium bond length for $H^{127}I$ is 1.604×10^{-10} m. Calculate the three lowest transition energies for the microwave (pure rotational) absorption spectroscopy and (ii) the two lowest Stokes Raman transition energies for the rotational Raman spectroscopy.

Solution 5.6 For this diatomic molecule, the reduced mass is given by

$$\mu = \frac{1.0078 \times 126.90}{1.0078 + 126.90} \times 1.6605 \times 10^{-24}\text{ g} = 1.6604 \times 10^{-24}\text{ g}.$$

For this reduced mass and the given internuclear distance, the rotational constant becomes $\tilde{B} = 6.553\ \text{cm}^{-1} = 1.302 \times 10^{-22}$ J. Thus, the three microwave absorption transition energies are as follows:

$$J(0 \rightarrow 1): \quad 2\tilde{B} = 13.11\ \text{cm}^{-1} = 2.604 \times 10^{-22}\ \text{J}$$
$$J(1 \rightarrow 2): \quad 4\tilde{B} = 26.21\ \text{cm}^{-1} = 5.206 \times 10^{-22}\ \text{J}$$
$$J(2 \rightarrow 3): \quad 6\tilde{B} = 39.32\ \text{cm}^{-1} = 7.810 \times 10^{-22}\ \text{J}$$

On the other hand, the two Stokes Raman transition energies are as follows:

$$J(0 \rightarrow 2): \quad 6\tilde{B} = 39.32\ \text{cm}^{-1} = 7.810 \times 10^{-22}\ \text{J}$$
$$J(1 \rightarrow 3): \quad 10\tilde{B} = 65.53\ \text{cm}^{-1} = 1.302 \times 10^{-21}\ \text{J}$$

5.7 For a diatomic molecule AlF, $\tilde{B}_0 = 0.55\ \text{cm}^{-1}$ and $\tilde{D}_e = 1.05 \times 10^{-6}\ \text{cm}^{-1}$. Calculate microwave absorption and Stokes Raman transition energies respectively for each case that the molecule has initial rotational quantum numbers $J = 1$ and $J = 5$.

Solution 5.7 This involves simple application of Eq. (5.132). Thus, the microwave absorption transition energies starting from $J = 1$ and $J = 5$ are as follows:

$$J(1 \rightarrow 2): \tilde{B}_0(6-2) - \tilde{D}_e(36-4) = 4\tilde{B}_0 - 32\tilde{D}_e$$
$$= 2.2\ \text{cm}^{-1} = 4.37 \times 10^{-23}\ \text{J}$$
$$J(5 \rightarrow 6): \tilde{B}_0(42-30) - \tilde{D}_e(1764-900) = 12\tilde{B}_0 - 864\tilde{D}_e$$
$$= 6.599\ \text{cm}^{-1} = 1.311 \times 10^{-22}\ \text{J}$$

On the other hand, the Stokes Raman transition energies starting from $J = 1$ and $J = 5$ are as follows:

$$J(1 \rightarrow 3): \tilde{B}_0(12-2) - \tilde{D}_e(144-4) = 10\tilde{B}_0 - 140\tilde{D}_e$$
$$= 5.5\ \text{cm}^{-1} = 1.09 \times 10^{-23}\ \text{J}$$
$$J(5 \rightarrow 7): \tilde{B}_0(56-30) - \tilde{D}_e(3136-900) = 26\tilde{B}_0 - 2236\tilde{D}_e$$
$$= 14.298\ \text{cm}^{-1} = 2.84 \times 10^{-22}\ \text{J}$$

5.8 For a diatomic molecule HCl, $\tilde{\nu}_e = 2885.9775\ \text{cm}^{-1}$, $\tilde{B}_e = 10.59342\ \text{cm}^{-1}$ and $\tilde{\alpha}_e = 0.30718\ \text{cm}^{-1}$ and assume that $\tilde{D}_e = 0$. Then, calculate the transition energies (in the unit of wavenumber cm^{-1}) for the first three P-branches and the first three R-branches.

Solution 5.8 This involves simple applications of Eqs. (5.136) and (5.137). Thus, the three P-branches are as follows:

$$\begin{aligned}
\tilde{\nu}_P(1) &= \tilde{\nu}_e - \tilde{\alpha}_e - 2(\tilde{B}_e - \tilde{\alpha}_e) \\
&= \tilde{\nu}_e + \tilde{\alpha}_e - 2\tilde{B}_e = 2865.09784 \text{ cm}^{-1}, \\
\tilde{\nu}_P(2) &= \tilde{\nu}_e - 4\tilde{\alpha}_e - 4(\tilde{B}_e - \tilde{\alpha}_e) \\
&= \tilde{\nu}_e - 4\tilde{B}_e = 2843.60382 \text{ cm}^{-1}, \\
\tilde{\nu}_P(3) &= \tilde{\nu}_e - 9\tilde{\alpha}_e - 6(\tilde{B}_e - \tilde{\alpha}_e) \\
&= \tilde{\nu}_e - 3\tilde{\alpha}_e - 6\tilde{B}_e = 2821.49544 \text{ cm}^{-1}.
\end{aligned}$$

On the other hand, the three R-branches are as follows:

$$\begin{aligned}
\tilde{\nu}_R(0) &= \tilde{\nu}_e + 2\tilde{B}_e - 3\tilde{\alpha}_e = 2906.2428 \text{ cm}^{-1}, \\
\tilde{\nu}_R(1) &= \tilde{\nu}_e - \tilde{\alpha}_e + (2\tilde{B}_e - 4\tilde{\alpha}_e) + (2\tilde{B}_e - 3\tilde{\alpha}_e) \\
&= \tilde{\nu}_e + 4\tilde{B}_e - 8\tilde{\alpha}_e = 2925.89374 \text{ cm}^{-1}, \\
\tilde{\nu}_R(2) &= \tilde{\nu}_e - 4\tilde{\alpha}_e + 4\tilde{B}_e - 8\tilde{\alpha}_e + 2\tilde{B}_e - 3\tilde{\alpha}_e \\
&= \tilde{\nu}_e - 15\tilde{\alpha}_e + 6\tilde{B}_e = 2944.93032 \text{ cm}^{-1}.
\end{aligned}$$

Problems

5.9 Prove that $[\hat{L}_x^2 + \hat{L}_y^2, \hat{L}_z] = 0$.

5.10 A three-dimensional rotor is in a rotational state $|\psi\rangle$ with the following wavefunction:

$$\psi(\theta, \phi) = \langle \theta, \phi | \psi \rangle = \psi(\theta) = A + \sqrt{\frac{1}{4\pi}} \cos\theta + \sqrt{\frac{15}{16\pi}} \cos^2\theta.$$

Determine A such that the above wavefunction is normalized. If $\hat{L}^2$ and $\hat{L}_z$ are measured for this state, what are possible outcomes and their probabilities?

5.11 A three-dimensional rotor is in a rotational state $|\psi\rangle$ with the following wavefunction:

$$\psi(\theta, \phi) = \langle \theta, \phi | \psi \rangle = \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta \cos\theta \cos\phi + i \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta \sin(2\phi).$$

If $\hat{L}^2$ and $\hat{L}_z$ are measured for this state, what are possible outcomes and their probabilities?

5.12 The ro-vibrational state of a diatomic molecule has the following term:

$$G(v, J) = \tilde{\nu}_e(v + \frac{1}{2}) + \tilde{B}_v J(J+1) - \tilde{D}_v J^2(J+1)^2,$$

where

$$\tilde{B}_v = \tilde{B}_e - \tilde{\alpha}_e \left(v + \frac{1}{2}\right),$$

$$\tilde{D}_v = \tilde{D}_e - \tilde{\delta}_e \left(v + \frac{1}{2}\right).$$

Find out expressions for P and R branches for the vibrational transition from $v = 0$ to $v = 1$.

Chapter 6
Hydrogen-Like Systems and Spin Orbit States of an Electron



When it comes to atoms, language can be used only as in poetry. The poet, too, is not nearly so concerned with describing facts as with creating images.

— Niels Bohr

Abstract This chapter provides detailed description of energies, states, and quantum numbers of the state of an electron in hydrogen-like systems, namely, hydrogen atom or ions with a single electron. First, Bohr's model is used for a simple derivation of energy levels. Then, the complete set of eigenfunctions and eigenvalues for the Hamiltonian as solutions of the time independent Schrödinger equation are provided. In particular, the equation for the radial part of the wavefunction and corresponding solutions are described in detail. Spin states of electron are then described, which in combination with spatial wavefunctions, namely, orbitals, provide full specification of a quantum state of an electron in a hydrogen-like system. Effects of a magnetic field on these states and consequences of spin-orbit interactions are briefly explained.

The hydrogen atom or hydrogen-like ion consists of only one nucleus with charge Z and an electron. The potential energy between the electron and the nucleus is the following Coulomb potential:

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}, \tag{6.1}$$

where $r = |\mathbf{r}_e - \mathbf{r}_n|$, with $\mathbf{r}_e$ and $\mathbf{r}_n$ being the positions of the electron and the nucleus respectively, $e = 1.602176634 \times 10^{-19}$ C, and $\epsilon_0 = 8.8541878128 \times 10^{-12}$ C^2/Nm, which is the electric permittivity of vacuum. Before we consider the solution of the Schrödinger equation for this potential, let us go over the Bohr's model first.

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6.1 Bohr's Model

Let us consider an electron, assumed to rotate around the nucleus with charge Z at a fixed distance r from the nucleus and with a constant speed v. This is possible only if the speed v of the electron is such that the Coulomb force balances the centrifugal force, which means that

$$\frac{Ze^2}{4\pi\epsilon_0 r^2} = \frac{m_e v^2}{r}. \tag{6.2}$$

This results in the following relationship between r and v:

$$r = \frac{Ze^2}{4\pi\epsilon_0 m_e v^2} = \frac{Zm_e e^2}{4\pi\epsilon_0 (m_e v)^2} = \frac{Zm_e e^2}{4\pi\epsilon_0 p_e^2}, \tag{6.3}$$

where $p_e = m_e v$ is the magnitude of the linear momentum of the electron. Information on r also determines the energy of the electron because

$$E = \frac{p_e^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r} = \frac{Ze^2}{8\pi\epsilon_0 r} - \frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{Ze^2}{8\pi\epsilon_0 r}. \tag{6.4}$$

On the other hand, according to de Broglie, p_e is inversely proportional to the wavelength of the electron as follows:

$$p_e = \frac{h}{\lambda_e}. \tag{6.5}$$

Having learned the principles and some details of the quantum mechanics and wavefunction, we can now view λ_e as the wavelength of electron's wavefunction defined along its circular trajectory. For the wave not to self-destruct itself along the trajectory with a periodic boundary condition, the integer multiples of the wavelength have to be equal to the circumference of the orbiting circle as follows:

$$n\lambda_e = 2\pi r, \; n = 1, 2, 3, \cdots . \tag{6.6}$$

In other words, if the above condition is not satisfied, there is no standing wave that is consistent with stable circular motion of the electron. Combining Eq. (6.6) with Eq. (6.5), we obtain the following relationship between p_e and r.

$$p_e = \frac{hn}{2\pi r} = \frac{\hbar n}{r}, \; n = 1, 2, 3, \cdots \tag{6.7}$$

Employing this expression in Eqs. (6.3) and (6.4), we find that

$$r_n = \frac{4\pi\epsilon_0\hbar^2 n^2}{Zm_e e^2} = \frac{n^2}{Z}a_0, \tag{6.8}$$

$$E_n = -\frac{m_e Z^2 e^4}{32\pi^2\epsilon_0^2\hbar^2 n^2} = -\frac{Z^2}{n^2}\frac{\hbar^2}{2m_e a_0^2}, \tag{6.9}$$

where $n = 1, 2, 3, \cdots$, and a_0 is the value of r_n for $Z = 1$ and $n = 1$. The expression for a_0 is as follows:

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529\ldots\ \text{Å}. \tag{6.10}$$

This is an important atomic constant known as the Bohr radius and is approximately equal to the size, namely, van der Waals radius, of a hydrogen atom. The constant factor, except for charge Z, in Eq. (6.9) is related to another important constant known as Rydberg constant given by

$$R_\infty = \frac{m_e e^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{hc} = \frac{m_e e^4}{8\epsilon_0^2 h^3 c} = \frac{\hbar}{4\pi m_e a_0^2 c} = 1.0974\cdots\times 10^5\ \text{cm}^{-1}. \tag{6.11}$$

As a result, the energy of the electron within the Bohr's model is expressed as

$$E_n = -R_\infty hc\frac{Z^2}{n^2}. \tag{6.12}$$

Energy levels given above turned out to be fairly accurate and were able to explain the electronic spectroscopic data of a hydrogen atom. It is even more amazing that Bohr was able to come up with the quantization condition, Eq. (6.6), before de Broglie's theory was proposed.

Equation (6.12) is based on the assumption that the position of the nucleus is fixed, which can be corrected by replacing the mass of an electron with the reduced mass for the system. For the case of a hydrogen atom, the reduced mass is $\mu = m_e m_H/(m_e + m_H)$. The resulting Rydberg constant for the electron in hydrogen atom is thus given by

$$R_H = \frac{\mu}{m_e}R_\infty = 1.0968\cdots\times 10^5\ \text{cm}^{-1}. \tag{6.13}$$

Therefore, the wavenumber of photons coming out of the (emission) transition between different states of the electron, according to the Bohr's model (with the correction of reduced mass), can be expressed as

$$\Delta\tilde{\nu}_{n_2\to n_1} = \frac{E_{n2} - E_{n1}}{hc} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right). \tag{6.14}$$

In fact, the above expression, known as Ritz combination principle, had already been well established experimentally before Bohr's model was developed. Specifically, the transitions to $n_1 = 1$ from any value of $n_2 > 1$ were known as Lyman series, those to $n_1 = 2$ from any value of $n_2 > 2$ Balmer series, and those to $n_1 = 3$ from any value of $n_2 > 3$ Paschen series. Bohr's model was able to explain these observations in a remarkably simple manner by magically combining particle and wave properties of the electron as described above. While the idea engrained in this Bohr's model formed the conceptual foundation of quantum mechanics, as will become clear, it is important to note that the success of Bohr's model as an accurate theory for energy levels of a hydrogen atom is due to the special nature of the Coulomb potential involved.

6.2 Solution of Schrödinger Equation

Hydrogen atoms or hydrogen-like ions are examples of two-particle system with their relative potential energy given by Eq. (6.1). Therefore, the Hamiltonian for their states and energies can be expressed in terms of the Hamiltonian given by Eq. (4.79). Let us assume that there is no external potential and that we are considering the hydrogen-like system in the center-of-mass coordinate system. Then, the Hamiltonian operator becomes

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2\mu} + \hat{V}(\hat{r}), \tag{6.15}$$

where $\mu = m_n m_e/(m_n + m_e)$, with m_n being the mass of the nucleus, and $\hat{\mathbf{p}} = \hat{\mathbf{p}}_e - \hat{\mathbf{p}}_n$ is the momentum of electron relative to the nucleus. When the above operator is applied to the position state represented as a bra in the Dirac notation, we obtain

$$\langle\mathbf{r}|\hat{H} = \left(-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right)\langle\mathbf{r}|. \tag{6.16}$$

This implies that the Schrödinger equation for the wavefunction $\psi(\mathbf{r}) = \langle\mathbf{r}|\psi\rangle$ is as follows:

$$\langle\mathbf{r}|\hat{H}|\psi\rangle = \left(-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{6.17}$$

From now one, for convenience, we will not strictly follow the convention of the Dirac notation and often express the first term in the above equation, simply as, $\hat{H}\psi(\mathbf{r})$, following the original Schrödinger's definition.

6.3 Separation of Variables in Spherical Coordinate System

As was shown in Chap. 5, the Laplacian ∇^2 in the spherical coordinate system is expressed as

$$\begin{aligned}\nabla^2 &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\\ &= \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}.\end{aligned} \tag{6.18}$$

Therefore, the Schrödinger equation, Eq. (6.17), in spherical coordinate system is expressed as

$$\hat{H}\psi(r,\theta,\phi) = \left(-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{2\mu r^2}\hat{L}^2 + V(r)\right)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi), \tag{6.19}$$

where $\hat{L}^2$ is the angular momentum operator defined in Chap. 5 and has the following expression:

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]. \tag{6.20}$$

This has the same form as that for the rotation of a diatomic molecule. However, in the present case, it is the angular momentum of (mostly) electron with respect to the center of mass, which is almost the same as the position of the nucleus.

We learned in Chap. 5 that the spherical harmonics are eigenfunctions of $\hat{L}^2$. Thus, we may be able to simplify Eq. (6.19) by assuming that the eigenfunction can be expressed as

$$\psi(r,\theta,\phi) = R(r)Y_l^{m_l}(\theta,\phi). \tag{6.21}$$

Note that we have used different labels for the quantum numbers of total angular momentum and the z-component angular momentum, l and m_l, in order to distinguish these from those for molecular rotations. Thus,

$$\hat{L}^2 Y_l^{m_l}(\theta,\phi) = \hbar^2 l(l+1)Y_l^{m_l}(\theta,\phi). \tag{6.22}$$

Employing the above identity in Eq. (6.19), we obtain

$$Y_l^{m_l}(\theta,\phi)\left[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}rR(r)+\frac{\hbar^2 l(l+1)}{2\mu r^2}R(r)+V(r)R(r)-ER(r)\right]=0. \tag{6.23}$$

The above equation is satisfied for arbitrary value of θ and ϕ if the equation within the square bracket is zero. Dividing the resulting equation with $-\hbar^2/(2\mu r)$, we thus obtain the following equation for the radial part of the eigenfunction:

$$\frac{d^2}{dr^2}(rR(r))+\left(\frac{2\mu E}{\hbar^2}-\frac{2\mu V(r)}{\hbar^2}-\frac{l(l+1)}{r^2}\right)(rR(r))=0. \tag{6.24}$$

The above equation is general and applicable to any potential energy $V(r)$. In the next subsection, we will consider the solution of this equation for the Coulomb potential.

6.3.1 *Radial Equation and Solution*

Employing the expression for the Coulomb potential, Eq. (6.1), in Eq. (6.24), we obtain

$$\frac{d^2}{dr^2}(rR(r))+\left(\frac{2\mu E}{\hbar^2}+\frac{2\mu Ze^2}{4\pi\epsilon_0\hbar^2 r}-\frac{l(l+1)}{r^2}\right)(rR(r))=0. \tag{6.25}$$

To simplify the above equation, let us introduce a scaled and dimensionless radial coordinate $\rho=\alpha_r r$, where α_r is yet unknown parameter with the unit of inverse length. Then, $d\rho=\alpha_r dr$. Let us also introduce $F(\rho)=R(r)$. Then, Eq. (6.25) is equivalent to

$$\frac{d^2}{d\rho^2}(\rho F(\rho))+\left(\frac{2\mu E}{\hbar^2\alpha_r^2}+\frac{2\mu Ze^2}{4\pi\epsilon_0\hbar^2\alpha_r}\frac{1}{\rho}-\frac{l(l+1)}{\rho^2}\right)(\rho F(\rho))=0. \tag{6.26}$$

The above equation can be simplified further by choosing α_r such that

$$\alpha_r=\frac{2\mu Ze^2}{4\pi\epsilon_0\hbar^2}=\frac{2}{a}, \tag{6.27}$$

where a is a generalization of the Bohr radius. For $Z=1$ and $\mu=m_e$, this becomes the Bohr radius a_0 defined by Eq. (6.10). Thus, employing this parameter, one can express Eq. (6.26) as follows:

$$\frac{d^2}{d\rho^2}(\rho F(\rho)) + \left(\frac{\mu a^2 E}{2\hbar^2} + \frac{1}{\rho} - \frac{l(l+1)}{\rho^2}\right)(\rho F(\rho)) = 0. \tag{6.28}$$

Solutions for the above equation can be found by first factoring out a term that becomes dominant at large ρ and then expanding the remaining function as a power series with respect to ρ. As detailed in the Appendix of this chapter, from the recursion relationship between coefficients of the power series expansion, one can show that physically well-behaving solutions exist only for the following values of the energy:

$$\frac{\mu a^2 E}{2\hbar^2} = -\frac{1}{4n^2}, \tag{6.29}$$

where n is a positive integer satisfying the following condition:

$$n \geq l + 1. \tag{6.30}$$

Appendix of this chapter also provides some examples of the resulting radial functions up to $n = 3$, with the lowest order coefficient C_0 as yet undetermined for each case. By determining the coefficient C_0 such that the following normalization constant is satisfied,

$$\int_0^\infty drr^2 R_{nl}(r) R_{n'l}(r) = \delta_{nn'}, \tag{6.31}$$

one can full specify the radial functions. Some examples of these expressions are provided in Table 6.1. Figure 6.1 provides plots of radial functions for $n = 0, \cdots, 4$ and $l = 0$, and Fig. 6.2 provides those for $n = 4$ and $l = 0, \cdots, 3$.

Table 6.1 Expressions for radial functions, $R_{nl}(r)$'s

n	l	$R_{nl}(r)$
1	0	$2\left(\frac{1}{a}\right)^{3/2} e^{-r/a}$
2	0	$\left(\frac{1}{2a}\right)^{3/2} \left(2 - \frac{r}{a}\right) e^{-r/(2a)}$
2	1	$\frac{1}{\sqrt{3}} \left(\frac{1}{2a}\right)^{3/2} \frac{r}{a} e^{-r/(2a)}$
3	0	$\frac{2}{27} \left(\frac{1}{3a}\right)^{3/2} \left(27 - 18\frac{r}{a} + 2\left(\frac{r}{a}\right)^2\right) e^{-r/(3a)}$
3	1	$\frac{1}{27} \left(\frac{2}{3a}\right)^{3/2} \left(\frac{r}{a}\right) \left(6 - \frac{r}{a}\right) e^{-r/(3a)}$
3	2	$\frac{4}{27\sqrt{10}} \left(\frac{1}{3a}\right)^{3/2} \left(\frac{r}{a}\right)^2 e^{-r/(3a)}$

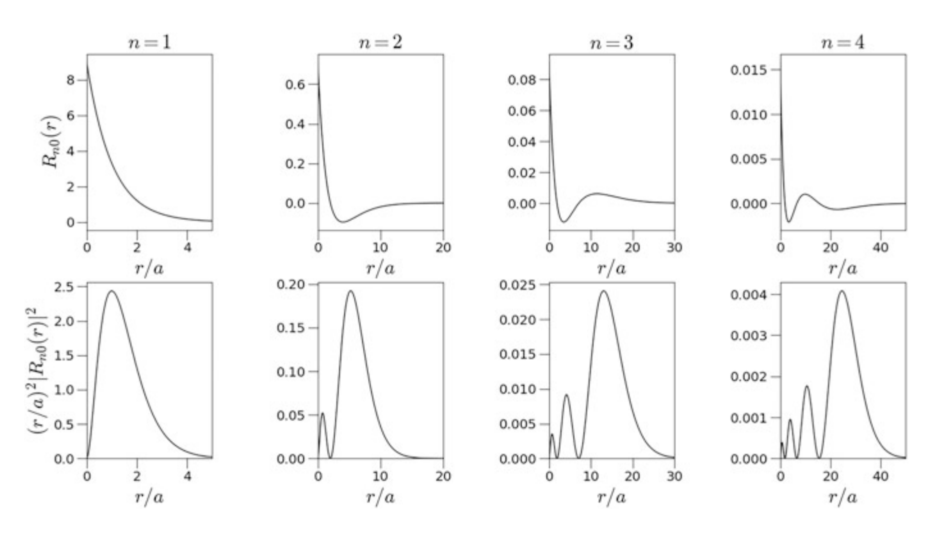


Fig. 6.1 Examples of four radial functions $R_{n0}(r)$ (upper panel) and $r^2|R_{n0}(r)|^2$ (lower panel), for n=1, 2, 3 ,and 4, versus r in the unit of a

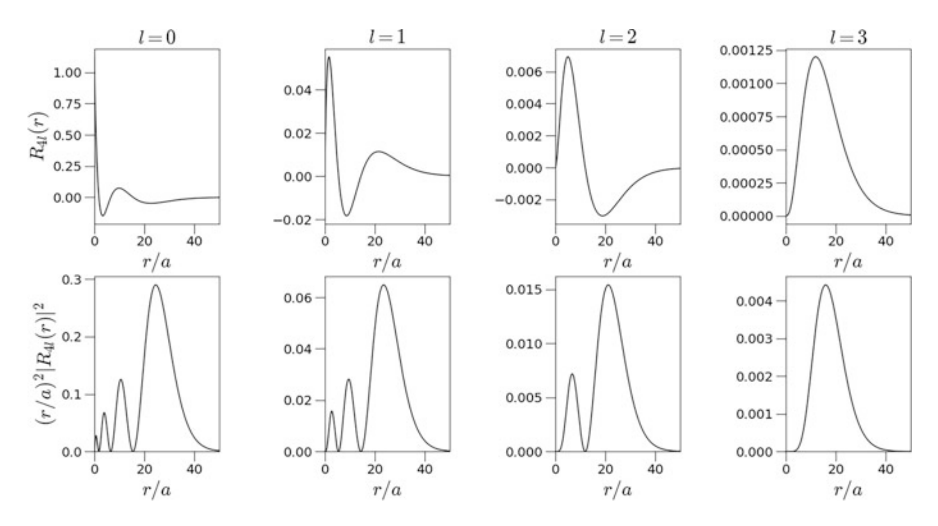


Fig. 6.2 Examples of four radial functions $R_{4l}(r)$ (upper panel) and $r^2|R_{4l}(r)|^2$ (lower panel), for l=0, 1, 2 ,and 3, versus r in the unit of a

While the solution of the radial equation provided in Appendix is straightforward, for a historical reason, the radial functions have been expressed more commonly in terms of associated Laguerre polynomials [23]. Thus, the radial functions are in general expressed as follows:

$$R_{nl}(r) = \left(\frac{(n-l-1)!}{2n[(n+l)!]^3}\right)^{1/2} \left(\frac{2}{na}\right)^{l+\frac{3}{2}} r^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right) e^{-r/(na)}, \tag{6.32}$$

where $L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)$ represents an associated Laguerre polynomial and is related to a Laguerre polynomial as follows:

$$L_n^k(x) = (-1)^k \frac{d^k}{dx^k} L_{n+k}(x). \tag{6.33}$$

In the above expression, $L_n(x)$ is the Laguerre polynomial of order n defined as

$$L_n(x) = \frac{e^x}{n!} \frac{d^n}{dx^n} \left(x^n e^{-x}\right), \tag{6.34}$$

and is a solution of the following Laguerre equation:

$$x \frac{d^2}{dx^2} f(x) + (1 - x) \frac{d}{dx} f(x) + n f(x) = 0. \tag{6.35}$$

6.3.2 Radial Probability Density

It is important to note that only the information on the radial function is needed to calculate the probability density to find the electron at a specific distance from the nucleus. The corresponding radial probability density is given by

$$P_{nl}(r) = r^2 [R_{nl}(r)]^2, \tag{6.36}$$

which satisfies the following normalization condition:

$$\int_0^\infty dr \, P_{nl}(r) = 1. \tag{6.37}$$

One can show that the average value of radius for each radial function is as follows:

$$\langle r \rangle_{nlm_l} = \int_0^\infty dr \, P_{nl}(r) r = a n^2 \left\{ 1 + \frac{1}{2} \left[1 - \frac{l(l+1)}{n^2} \right] \right\}. \tag{6.38}$$

As an example, consider the case where $n = 1$ and $l = 0$, for which

$$P_{10}(r) = \frac{4}{a^3} r^2 e^{-2r/a}. \tag{6.39}$$

Taking the derivative of this with respect to r, we can determine the most likely value of r by using the following condition:

$$\frac{d}{dr} P_{10}(r) = \frac{4}{a^3} \left(2r e^{-2r/a} - \frac{2r^2}{a} e^{-2r/a} \right) = 0. \tag{6.40}$$

The above equation is satisfied for $r = a$. In other words, a is the value of the radius for which the state with $n = 1$ and $l = 0$ has the maximum probability. The radial probability can also be used to determine the average potential energy as follows:

$$\begin{aligned}\langle V(r)\rangle_{10} &= \int_0^\infty dr P_{10}(r)\left(-\frac{e^2}{4\pi\epsilon_0 r}\right)\\ &= -\frac{e^2}{4\pi\epsilon_0}\frac{4}{a^3}\int_0^\infty drre^{-2r/a} = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{a} = -\frac{\hbar^2}{m_e}\frac{1}{a^2} = 2E_1.\end{aligned} \tag{6.41}$$

The above result shows that the average potential energy is equal to the value of the potential at the most probable value of r, an outcome specific for $1/r$ dependence of the potential energy. This also explains why the simple Bohr's model, which relied on classical-like relationship employing the most probable value of r, was successful in reproducing the experimental data.

6.3.3 Eigenfunctions and Eigenstates in the Dirac Notation

Combining the radial function with the spherical harmonics, we can now write down the full eigenfunction of $\hat{H}$ for each eigenvalue.

Eigenfunctions for a Hydrogen-Like System

The eigenfunction for the electron in a hydrogen atom or hydrogen-like ion with nuclear charge Z is

$$\psi_{nlm_l}(r,\theta,\phi) = R_{nl}(r)Y_l^{m_l}(\theta,\phi). \tag{6.42}$$

This satisfies the following Schrödinger equation:

$$\left(-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{2\mu r^2}\hat{L}^2 - \frac{Ze^2}{4\pi\epsilon_0 r}\right)\psi_{nlm_l}(r,\theta,\phi) = E_n\psi_{nlm_l}(r,\theta,\phi), \tag{6.43}$$

where $\hat{L}^2$ is the angular momentum operator given by Eq. (6.20) and E_n is the eigenvalue of the Hamiltonian given by

$$E_n = -\frac{\hbar^2}{2\mu a^2}\frac{1}{n^2} = -\frac{\mu Z^2 e^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2}. \tag{6.44}$$

(continued)

All the eigenfunctions defined by Eq. (6.42) satisfy the following orthonormality condition:

$$\int_0^\infty dr r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi\, \psi_{n'l'm_{l'}}(r,\theta,\phi)\psi_{nlm_l}(r,\theta,\phi) = \delta_{nn'}\delta_{ll'}\delta_{m_l m_l'}. \tag{6.45}$$

Having identified all the eigenfunctions of $\hat{H}$, it is now convenient to introduce the eigenstate in the Dirac notation, $|n,l,m\rangle$, which is defined through the following relationship:

$$\psi_{nlm_l}(r,\theta,\phi) = \langle \mathbf{r}|n,l,m_l\rangle. \tag{6.46}$$

Since $\int d\mathbf{r}\ |\mathbf{r}\rangle\langle\mathbf{r}| = \hat{1}$, the identity operator, the above definition along with Eq. (6.45) implies that

$$\langle n',l',m_{l'}|n,l,m_l\rangle = \delta_{nn'}\delta_{ll'}\delta_{m_l m_{l'}}. \tag{6.47}$$

Employing these, all the results obtained so far can be expressed succinctly in the Dirac notation as summarized below.

Eigenstates in the Dirac Notation

For the eigenvalue E_n given by Eq. (6.44), there is an eigenstate $|n,l,m_l\rangle$ that satisfies the following identities:

$$\hat{H}_{rel}|n,l,m_l\rangle = \left(\frac{\hat{\mathbf{p}}^2}{2\mu} - \frac{Ze^2}{4\pi\epsilon_0\hat{r}}\right)|n,l,m_l\rangle = E_n|n,l,m_l\rangle, \tag{6.48}$$

$$\hat{L}^2|n,l,m_l\rangle = \hbar^2 l(l+1)|n,l,m_l\rangle, \tag{6.49}$$

$$\hat{L}_z|n,l,m_l\rangle = \hbar m_l|n,l,m_l\rangle, \tag{6.50}$$

where $l = 0,\cdots,n-1$ and $m_l = -l,\cdots,l$.

The fact that $[\hat{H}_{rel},\hat{L}^2] = 0$ and $[\hat{H}_{rel},\hat{L}_z] = 0$ explains why there is a simultaneous eigenstate of the three operators, $\hat{H}_{rel}$, $\hat{L}^2$, and $\hat{L}_z$, which is $|n,l,m_l\rangle$ shown above. The set of numbers (n,l,m_l) is called good quantum numbers, which represent a set of compatible quantum numbers representing conserved quantities. In this set, n is called the principal quantum number, l is called the angular

momentum quantum number, and m_l is the magnetic quantum number. The value of l is also often represented by the symbols shown below.

Symbols for Angular Momentum Quantum Numbers

l	0	1	2	3	4
	s	p	d	f	g

6.3.4 *Zeeman Effect*

In the absence of an external field, all the states with different values of l and m_l for the same value of n are degenerate. On the other hand, states with different values of m_l have different values of energy in the presence of a magnetic field, which is typically assumed to be in the z-direction. This is called Zeeman effect and is the reason why m_l is called magnetic quantum number.

In the presence of a magnetic field, the potential energy of system with magnetic moment is given by

$$V = -\mathbf{m}_L \cdot \mathbf{B}. \tag{6.51}$$

where $\mathbf{m}_L$ is the magnetic moment vector with its magnitude defined as follows:

$$\begin{aligned} |\mathbf{m}_L| &= \text{Current} \times \text{Area surrounded by current} \\ &= I \cdot \pi r^2 = \frac{qv}{2\pi r}\pi r^2 = \frac{1}{2}qrv. \end{aligned} \tag{6.52}$$

In a vector notation, the magnetic moment is given by

$$\mathbf{m}_L = \frac{q}{2m}\mathbf{r} \times \mathbf{p} = \frac{q}{2m}\mathbf{L}. \tag{6.53}$$

For an electron,

$$\mathbf{m}_L = -\frac{e}{2m_e}\mathbf{L}, \tag{6.54}$$

where $\mathbf{L}$ is the angular momentum of the electron. Thus, in the presence of a magnetic field $\mathbf{B} = B_z\mathbf{e}_z$, the potential energy of the electron due to the magnetic

field is given by

$$V = -\left(-\frac{e}{2m_e}\mathbf{L}\right)\cdot\mathbf{B} = \frac{eB_z}{2m_e}L_z = \frac{\beta_B}{\hbar}B_z L_z, \tag{6.55}$$

where $\beta_B = e\hbar/(2m_e)$ and is called Bohr magneton. Thus, in the presence of the magnetic field, the total Hamiltonian is given by

$$\hat{H}_B = \hat{H}_{rel} + \frac{\beta_B}{\hbar}B_z\hat{L}_z. \tag{6.56}$$

Since $[\hat{H}_{rel}, \hat{L}_z] = 0$, the eigenstate of $\hat{H}_{rel}$, $|n, l, m_l\rangle$ still remains the eigenstate of $\hat{H}_B$. The only difference is that the eigenvalue now becomes

$$E_{n,m_l} = -\frac{\hbar^2}{2\mu a^2}\frac{1}{n^2} + \beta_B B_z m_l. \tag{6.57}$$

This expression provides quantitative details of the Zeeman effect, and shows that the energy splitting is proportional to both m_l and B_z.

6.3.5 Real-Valued Orbital Functions

As mentioned above, $|n, l, m_l\rangle$ or $\psi_{nlm_l}(r, \theta, \phi)$ has the same energy in the absence of external field as long as n remains the same. Thanks to this degeneracy, any linear combination of $Y_l^{m_l}(\theta, \phi)$ for the same l can serve as simultaneous eigenstate of the Hamiltonian $\hat{H}_{rel}$ and $\hat{L}^2$. Namely, the following linear combination leads to another eigenstate of the same eigenvalue.

$$R_{nl}(r)Y_l^{m_l}(\theta, \phi) \rightarrow R_{nl}(r)\left(\sum_{m_l} C_{m_l}Y_l^{m_l}(\theta, \phi)\right). \tag{6.58}$$

This fact can be used to create real functions out of complex valued $Y_l^{m_l}(\theta, \phi)$'s. For example, for $l = 1$, out of

$$Y_1^1(\theta, \phi) = -\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{i\phi}, \tag{6.59}$$

$$Y_1^{-1}(\theta, \phi) = \left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{-i\phi}, \tag{6.60}$$

one can create

$$p_x = \frac{1}{\sqrt{2}}\left(Y_1^{-1}(\theta,\phi) - Y_1^{1}(\theta,\phi)\right) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi, \tag{6.61}$$

$$p_y = \frac{i}{\sqrt{2}}\left(Y_1^{-1}(\theta,\phi) + Y_1^{1}(\theta,\phi)\right) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi. \tag{6.62}$$

Along with p_z defined as

$$p_z = Y_1^0(\theta,\phi) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta, \tag{6.63}$$

p_x and p_y given by Eqs. (6.61) and (6.62) form orthonormal and real eigenfunctions of $\hat{L}^2$. However, note that these are no longer eigenfunctions of $\hat{L}_z$. Similarly, for $l = 2$, one can form the following five real valued angular functions:

$$d_{z^2} = Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2}\left(3\cos^2\theta - 1\right), \tag{6.64}$$

$$d_{xz} = \frac{1}{\sqrt{2}}\left(Y_2^{-1} - Y_2^{1}\right) = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\cos\phi, \tag{6.65}$$

$$d_{yz} = \frac{i}{\sqrt{2}}\left(Y_2^{-1} + Y_2^{1}\right) = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\sin\phi, \tag{6.66}$$

$$d_{x^2-y^2} = \frac{1}{\sqrt{2}}\left(Y_2^{2} + Y_2^{-2}\right) = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\cos 2\phi, \tag{6.67}$$

$$d_{yz} = \frac{i}{\sqrt{2}}\left(Y_2^{-2} - Y_2^{2}\right) = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\sin 2\phi, \tag{6.68}$$

All of the above functions are orthonormal and are eigenfunctions of $\hat{L}^2$. However, except for d_{z^2}, none is the eigenfunction of $\hat{L}_z$ any more.

6.4 Spin States

Imagine a particle circling around a circle of radius r with speed v. Assume that $r \to 0$ while $|\mathbf{v}| \propto 1/r$. In this limit, the particle spins around itself with infinitely fast speed, but with finite angular momentum. The angular momentum in this limiting case can be called spin. However, one should be careful because this is just an analogy. Quantum mechanical spin cannot be visualized like an orbital angular momentum wavefunction. On the other hand, it still behaves almost like

conventional angular momentum with respect to the rotational transformation of the space. As a consequence, they satisfy the same commutation relations as angular momentum operators.

Commutation Relations and Eigenvalues of Spin Operators

The three components of the spin operator satisfy the following commutator relations:

$$[\hat{S}_x, \hat{S}_y] = i\hbar \hat{S}_z, \tag{6.69}$$

$$[\hat{S}_y, \hat{S}_z] = i\hbar \hat{S}_x, \tag{6.70}$$

$$[\hat{S}_z, \hat{S}_x] = i\hbar \hat{S}_y. \tag{6.71}$$

Thus, the spin state can be specified in terms of $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$ and $\hat{S}_z$. The eigenvalues of these operators are given by $S(S+1)$ and $\hbar m_s$, where $S \geq |m_s|$. The Dirac notation is very convenient for describing these spin states. Namely, the spin eigenstates are defined as follows:

$$\hat{S}^2|S, m_s\rangle = \hbar^2 S(S+1)|S, m_s\rangle, \tag{6.72}$$

$$\hat{S}_z|S, m_s\rangle = \hbar m_s|S, m_s\rangle. \tag{6.73}$$

There are two major differences between the spin and the spatial angular momentum as stated below.

- Spin is a unique intrinsic property of a particle like its mass.
- The total spin quantum number S can be half integers as well as full integers.

Particles with a half integer value of S have properties distinctively different from those with a full integer value of S. The former type of particle is called fermion (named after Fermi) and the latter is called boson (named after Bose).

Well known examples of fermions are electron, proton, and neutron, which all have $S = 1/2$. Well known examples of bosons are photon and deuteron, which all have $S = 1$. Fermions cannot share a quantum state, which is specified by the all compatible orbital quantum numbers and the spin state. On the other hand, there is no limit in the number of bosons that can occupy the same state. Therefore, at zero or near zero temperature, bosons tend to occupy the ground state, which is called Bose-Einstein condensation.

Since the spin of an electron is $1/2$, it is a fermion and has the following two spin states:

$$|\alpha\rangle \equiv \left|\frac{1}{2}, \frac{1}{2}\right\rangle = \left|\frac{1}{2}\right\rangle, \tag{6.74}$$

$$|\beta\rangle \equiv \left|\frac{1}{2}, -\frac{1}{2}\right\rangle = \left| -\frac{1}{2}\right\rangle, \tag{6.75}$$

where the second equality is an abbreviation typically used because $S = 1/2$ remains constant for electron. By definition, $\langle\alpha|\alpha\rangle = 1$, $\langle\beta|\beta\rangle = 1$, and $\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$. Combining the above spin states of an electron with those for spatial orbitals, we can define the following two states:

$$\left|n, l, m_l, \frac{1}{2}\right\rangle = |n, l, m_l\rangle|\alpha\rangle = |n, l, m_l\rangle \otimes |\alpha\rangle, \tag{6.76}$$

$$\left|n, l, m_l, -\frac{1}{2}\right\rangle = |n, l, m_l\rangle|\beta\rangle = |n, l, m_l\rangle \otimes |\beta\rangle, \tag{6.77}$$

where $\otimes$ represent the direct product, which amounts to expanding the state space as explained in Chap. 2. Note that this kind of direct product is possible between two sets of states corresponding to independent variables. Another example of direct product is $|\mathbf{r}\rangle = |x\rangle \otimes |y\rangle \otimes |z\rangle = |x\rangle|y\rangle|z\rangle$. As can be seen from these definitions, direct product symbols are often omitted unless there is any source of confusion.

Taking inner products of Eqs. (6.76) and (6.77) with a position state, we also obtain

$$\left\langle\mathbf{r}|n, l, m_l, \frac{1}{2}\right\rangle = \langle\mathbf{r}|n, l, m_l\rangle|\alpha\rangle = \psi_{nlm_l}(r, \theta, \phi)|\alpha\rangle, \tag{6.78}$$

$$\left\langle\mathbf{r}|n, l, m_l, -\frac{1}{2}\right\rangle = \langle\mathbf{r}|n, l, m_l\rangle|\beta\rangle = \psi_{nlm_l}(r, \theta, \phi)|\beta\rangle. \tag{6.79}$$

The spin of an electron also interacts with a magnetic field through its magnetic moment defined as follows:

$$\mathbf{m}_s = -\frac{ge}{2m_e}\mathbf{S}, \tag{6.80}$$

where $g = 2.002319\ldots$ and is called anomalous spin factor. Therefore, in the presence of a magnetic field along the z-direction, the potential of the electron is

$$V = -(\mathbf{m}_L + \mathbf{m}_s) \cdot \mathbf{B} = \frac{e}{2m_e}(\mathbf{L} + g\mathbf{S}) \cdot \mathbf{B} = \frac{\beta_B}{\hbar} B_z(L_z + gS_z). \tag{6.81}$$

Therefore, the total Hamiltonian for an electron in a hydrogen-like system subject a magnetic field is

$$\hat{H} = \hat{H}_{rel} + \frac{\beta_B}{\hbar} B_z(\hat{L}_z + g\hat{S}_z). \tag{6.82}$$

States given by Eqs. (6.76) and (6.77) (or Eqs. (6.78) and (6.79) in position representation) can be shown to be eigenstates of the above Hamiltonian, and the corresponding eigenvalues are

$$E_{n,m_l,m_s} = -\frac{\hbar^2}{2\mu a_0^2}\frac{1}{n^2} + \beta_B B_z (m_l + g m_s). \tag{6.83}$$

While the above effect is easy to understand, the fact that electron is in a frame that continuously accelerates causes another effect of spin on the energy of the electron in hydrogen-like system even when there is no magnetic field. The reason is that the electron sees the nucleus as accelerating and therefore experiences the magnetic field caused by its motion. This magnetic field then interacts with the spin of the electron. Thus, the true Hamiltonian of the electron in a hydrogen-like system should be expressed as

$$\hat{H} = \hat{H}_{rel} + \xi(r)\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \tag{6.84}$$

where $\xi(r)$ is a function that depends on the distance between the nucleus and the electron. Solving the Schrödinger equation for this Hamiltonian is more difficult if not impossible. On the other hand, the above form gives insight into what should be good quantum numbers when the spin-orbit interaction is included.

Let us define the sum of the orbital angular momentum and the spin as follows:

$$\mathbf{J} = \mathbf{L} + \mathbf{S}. \tag{6.85}$$

Then, it is clear that

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2}\left\{(\mathbf{L} + \mathbf{S})^2 - \mathbf{L}^2 - \mathbf{S}^2\right\} = \frac{1}{2}\left\{\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2\right\}. \tag{6.86}$$

Thus,

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2}\left\{\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2\right\}. \tag{6.87}$$

Therefore, the spin-orbit coupling can be determined once we know all three eigenvalues of $\hat{\mathbf{J}}^2$, $\hat{\mathbf{L}}^2$, and $\hat{\mathbf{S}}^2$. For this, let us consider the z-component of $\hat{\mathbf{J}}$ given by

$$\hat{J}_z = \hat{L}_z + \hat{S}_z. \tag{6.88}$$

Since the eigenvalue of $\hat{S}_z$ for an electron is $\pm 1/2$, the eigenvalue of $\hat{J}_z$ is expected to be

$$j_z = m_l \pm \frac{1}{2}, \tag{6.89}$$

where $m_l = -l, \cdots, l$. This means that the maximum magnitude of j_z is $l - 1/2$ or $l + 1/2$ depending on the value of spin. Otherwise, the eigenvalue of $\hat{\mathbf{J}}^2$ has the same structure as $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{S}}^2$ as follows:

$$\hat{\mathbf{J}}^2 \rightarrow \hbar^2 j(j+1), \text{ where } j = l \pm \frac{1}{2}. \tag{6.90}$$

Note that, for the case where $l = 1/2$, only $j = 1/2$ is possible.

6.5 Electronic Transitions and Term Symbols

In an electronic transition of a hydrogen-like system due to linear interaction with light (single photon transition), the following selection rules apply.

Selection Rules of Electronic Transitions in Hydrogen-Like Systems

$$\Delta l = \pm 1, \tag{6.91}$$

$$\Delta S = 0, \tag{6.92}$$

$$\Delta j = 0, \pm 1 \text{ (No } 0 \rightarrow 0 \text{ transition).} \tag{6.93}$$

The orbital angular momentum selection rule, Eq. (6.91), can be understood from the fact that (1) the total angular momentum of the electron plus the spin of photon, which is equal to one, has to be conserved and (2) that the transition is possible only between states with different odd/even symmetry with respect to the inversion of the space. This latter rule exists because the interaction with light occurs through the dipole operator, which has odd spatial symmetry. Due to this constraint, $\Delta l = 0$ is not possible.

The spin selection rule, Eq. (6.92), results from the fact that the spin of an electron does not interact with the electric field of the radiation. Finally, Eq. (6.93) can be understood from the fact that $\mathbf{J} = \mathbf{L} + \mathbf{S}$. Even though $\Delta l = 0$ is not possible, $\Delta j = 0$ can occur through the contribution of the spin having a direction different from that of the orbital angular momentum.

Although this chapter is focused on a hydrogen-like system with only one electron, it is useful to introduce here more general term symbols used for describing many electron atoms as described below.

Definition of Atomic Term Symbols

Atomic term symbols provide compact ways to represent the angular momentum, spin, and sum of the two, for electrons in an atom, and are expressed as

$$^{2S+1}\mathrm{T}_J, \tag{6.94}$$

where T = S (for $L = 0$), P (for $L = 1$), D (for $L = 2$), ... Namely, these are capital letters for the symbols used for hydrogen-like orbital functions. The left superscript denotes the spin multiplicity $2S + 1$, and the right subscript is the value of J.

For a hydrogen-like system, $2S + 1 = 2$. Thus, possible electronic term symbols for a hydrogen-like system are as follows:

$$^2\mathrm{S}_{1/2}, ^2\mathrm{P}_{1/2}, ^2\mathrm{P}_{3/2}, ^2\mathrm{D}_{3/2}, ^2\mathrm{D}_{5/2}, \cdots \tag{6.95}$$

For the consideration of many-electron systems in the next chapter, it is also useful to introduce the general rule of angular momentum addition here. Classically, when two angular momenta, $\mathbf{L}_1$ and $\mathbf{L}_2$, are added to become $\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2$, possible magnitudes of $\mathbf{L}$ are in the following range:

$$||\mathbf{L}_1| - |\mathbf{L}_2|| \leq |\mathbf{L}| \leq |\mathbf{L}_1| + |\mathbf{L}_2|. \tag{6.96}$$

Quantum mechanically, this condition remains true except that the quantization condition has to be satisfied as well. That is, the eigenvalue of $\hat{L}^2$ is as follows:

$$\hat{\mathbf{L}}^2 \rightarrow \hbar^2 L(L+1), L = |L_1 - L_2|, |L_1 - L_2| + 1, \cdots, L_1 + L_2 - 1, L_1 + L_2, \tag{6.97}$$

where L_1 is a quantum number for $\hat{L}_1^2$, for which the corresponding eigenvalue is $\hbar^2 L_1(L_1 + 1)$, and L_2 is that for $\hat{L}_2^2$, for which the eigenvalue is $\hbar L_2(L_2 + 1)$. Because the above identity is related to the symmetry property of the angular momentum operator, the same relation holds for spin and the total angular momentum (the sum of spin and orbital angular momentum) as well. Namely, for $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$,

$$\hat{\mathbf{S}}^2 \rightarrow \hbar^2 S(S+1) \text{ , with } S = |S_1 - S_2|, \cdots, S_1 + S_2, \tag{6.98}$$

where S_1 and S_2 are quantum numbers for $\hat{S}_1^2$ and $\hat{S}_2^2$, which respectively have eigenvalues $\hbar^2 S_1(S_1+1)$ and $\hbar S_2(S_2+1)$. The same relation also holds for $\mathbf{J} = \mathbf{L}+\mathbf{S}$ as follows:

$$\hat{\mathbf{J}}^2 \rightarrow \hbar^2 J(J+1) \text{ , with } J = |L-S|, \cdots, L+S, \tag{6.99}$$

where L and S are quantum numbers for $\hat{L}^2$ and $\hat{S}^2$, which respectively have eigenvalues $\hbar^2 L(L+1)$ and $\hbar S(S+1)$.

6.6 Summary and Questions

Quantized energy levels of an electron in a hydrogen-like system, according to Bohr's model, can be explained assuming a classical-like motion of the electron orbiting around the nucleus, and requiring only one additional condition. It is to assume that the circular orbit of the electron is an integer multiple of its de Broglie wavelength, which in turn can be calculated by the value of the momentum that maintains the balance between the centrifugal force and the Coulomb attraction by the nucleus. The resulting expression is Eq. (6.12), which becomes exact if the mass of an electron is replaced with the reduced mass for the system.

The success of Bohr's model indicates that the physical origin of the quantized energy levels of an electron is the periodic nature of its motion. Bohr's model captures this in the simplest manner by incorporating the duality of a particle-like property and a wave-like nature of the electron into the requirement of energy conservation described in a classical manner.

For more complete description of the electron, a complete solution of the time independent Schrödinger equation is necessary. This becomes possible by using a spherical coordinate system and employing the solution for the rotational part, the spherical harmonics, to derive an equation for the radial part, Eq. (6.25). This equation can be solved exactly, resulting in radial functions shown in Table 6.1 as examples. A general expression involving Laguerre function and an exponential function is given by Eq. (6.32). Combination of this with the spherical harmonics results in the full expression for the eigenfunction, Eq. (6.42), for which the eigenvalue is given by Eq. (6.44). Alternatively, these can be expressed in the Dirac notation as $|n, l, m_l\rangle$, which represents a simultaneous eigenstate of the the Hamiltonian, the square of the angular momentum, and the z-component of the angular momentum according to Eqs. (6.48)–(6.50).

Because an electron has a spin of magnitude $\hbar/2$, for which there can be two spin states, up and down, as shown in Eqs. (6.74) and (6.75), a complete specification of the quantum state of an electron requires consideration of both the spin and spatial orbital states, as shown in Eqs. (6.76) and (6.77). Although many of these states are degenerate, having the same energy for the same principal quantum number, application of an external magnetic field can easily lift such degeneracy

since the corresponding eigenvalue is given by Eq. (6.83). At finer scale, it turns out that further complications arise due to spin-orbit effects for example. A heuristic description of the spin-orbit effects has been provided, which shows that the information on the sum of the orbital angular momentum and the spin is needed for complete specification of the eigenstate. In fact, the corresponding quantum number, normally denoted as J turns out to be important in general and serves as an important quantum number for fully specifying many electron states as well as a single electron state. The atomic term symbol given by Eq. (6.94) conveys this information succinctly.

Selection rules for electronic transitions involving interaction of an electron with one photon are provided by Eqs. (6.91)–(6.93). Term symbols are introduced in order to make the description of these electronic transitions in a succinct manner and also for the consideration of more general many-electron states that will be treated in the next chapter.

Questions

- Bohr's model can predict exact energy levels of an electron in a hydrogen-like system despite its simplicity. How is this possible?
- Energy levels of an electron in a hydrogen-like system are independent of the orbital angular momentum quantum number? Why does such independence occur despite that the radial equation in fact depends on the orbital angular momentum quantum number?
- For eigenfunctions of the electron in a hydrogen-like system, what is the sum of the number of radial nodes in the radial function and that of nodal planes in the angular part of the eigenfunction? How does it depend on the principal quantum number and angular momentum quantum number?
- For a given principal quantum number, does the increase of the orbital angular momentum quantum number make the average distance between the electron and the nucleus larger or smaller?
- For a given principal quantum number, does the increase of the orbital angular momentum quantum number make the probability of finding the electron near the nucleus higher or lower?
- What is the common property of the orbital angular momentum and the spin of an electron and what are major differences?
- What causes the coupling between the spin and the orbit angular momentum of an electron in a hydrogen-like system?
- In the transition of the electronic energy level in a hydrogen-like system due to emission or absorption of one photon, the orbital angular momentum quantum number does not remain the same. What is the reason for this?

Appendix: Solutions of the Radial Equation

We here consider in more detail the solution of Eq. (6.28) for the bound state $E < 0$. Let us introduce

$$\gamma = \sqrt{-\frac{\mu a^2 E}{2\hbar^2}}, \tag{6.100}$$

and another function $G(\rho)$ such that

$$\rho F(\rho) = e^{-\gamma\rho} G(\rho). \tag{6.101}$$

Then,

$$\frac{d^2}{d\rho^2}\left(\rho F(\rho)\right) = e^{-\gamma\rho}\left(\gamma^2 G(\rho) - 2\gamma\frac{d}{d\rho}G(\rho) + \frac{d^2}{d\rho^2}G(\rho)\right). \tag{6.102}$$

Using Eqs. (6.101) and (6.102) in Eq. (6.28) and factoring out $e^{-\gamma\rho}$, we find that

$$\frac{d^2}{d\rho^2}G(\rho) - 2\gamma\frac{d}{d\rho}G(\rho) + \left(\frac{1}{\rho} - \frac{l(l+1)}{\rho^2}\right)G(\rho) = 0. \tag{6.103}$$

Now let us assume that

$$G(\rho) = \sum_{k=0}^{\infty} C_k \rho^{k+p}, \tag{6.104}$$

where p and C_k's need to be determined so as to satisfy Eq. (6.103). Using the above expression and its first and second derivatives with respect to ρ in Eq. (6.103), we obtain

$$\sum_{k=0}^{\infty}\Big\{C_k(k+p)(k+p-1)\rho^{k+p-2} - 2\gamma C_k(k+p)\rho^{k+p-1} + C_k\rho^{k+p-1} - C_k l(l+1)\rho^{k+p-2}\Big\} = 0. \tag{6.105}$$

Rearranging terms, the above equation can be expressed as

$$C_0\left(p(p-1) - l(l+1)\right)\rho^{p-2} + \sum_{k=0}^{\infty}\left\{C_{k+1}\left((k+p+1)(k+p) - l(l+1)\right) - C_k\left(2\gamma(k+p) - 1\right)\right\}\rho^{k+p-1} = 0. \tag{6.106}$$

From the first term in the above equation, we obtain the following condition for p:

$$p(p-1) - l(l+1) = (p+l)(p-l-1) = 0. \tag{6.107}$$

Thus, $p = -l$ or $l + 1$. For nonzero l, the former case results in a function that cannot be normalized due to the singularity at $r = 0$. For $l = 0$, the solution with $p = 0$ still appears to be possible because it leads to a normalizable wavefunction. However, when this function is included as one of the basis function, the resulting kinetic energy operator is no longer Hermitian. Therefore, all cases with $p = -l$ should be excluded and we can use the latter option of $p = l + 1$ only.

On the other hand, for the summation in Eq. (6.106) to be zero, the following recursion relation has to be satisfied.

$$C_{k+1} = \frac{2\gamma(k+p) - 1}{(k+p+1)(k+p) - l(l+1)} C_k. \tag{6.108}$$

Let us first assume that the series do not terminate and C_k's remain nonzero for all k. Then, in the large k limit of $k >> l, p$,

$$C_{k+1} \approx \frac{2\gamma}{(k+1)} C_k. \tag{6.109}$$

This means that $G(\rho) \sim e^{2\gamma\rho}$ for large ρ, which again means that $\rho F(\rho) \sim e^{\gamma\rho}$. This is an unphysical solution. Therefore, the series has to terminate at some finite order, which is possible as long as the following condition for some $k \geq 0$ is satisfied.

$$\gamma = \frac{1}{2(k+p)} = \frac{1}{2(k+l+1)}, \qquad k = 0, 1, 2, \cdots \tag{6.110}$$

In the second equality of the above expression, we have used the fact that $p = l + 1$. Now let us introduce

$$n = k + l + 1, \qquad k = 0, 1, 2, \cdots \tag{6.111}$$

Then, $n \geq l + 1$ and Eq. (6.110) implies that

$$\gamma = \frac{1}{2n}. \tag{6.112}$$

Combining this with the definition of γ given by Eq. (6.100), we obtain the following expression for the energy:

$$E_n = -\frac{\hbar^2}{2\mu a^2} \frac{1}{n^2}, \qquad n = 1, 2, \cdots \tag{6.113}$$

where n was also used as a subscript to label each energy.

For a given $n = k_{max} + l + 1$ and $l = p - 1$, the recursion relation, Eq. (6.108), can be expressed as

$$C_{k+1} = -\frac{n-k-l-1}{n(k+1)(k+2l+2)} C_k, \qquad k = 0, \cdots, k_{max} \tag{6.114}$$

Using this recursion relationship, it is straightforward to find expressions for all of the $G_{nl}(\rho)$, some of which are listed below.

$$G_{10}(\rho) = C_0 \rho, \tag{6.115}$$

$$G_{20}(\rho) = C_0 \rho \left(1 - \frac{\rho}{4}\right), \tag{6.116}$$

$$G_{21}(\rho) = C_0 \rho^2, \tag{6.117}$$

$$G_{30}(\rho) = C_0 \rho \left(1 - \frac{1}{3}\rho + \frac{1}{54}\rho^2\right), \tag{6.118}$$

$$G_{31}(\rho) = C_0 \rho^2 \left(1 - \frac{1}{12}\rho\right), \tag{6.119}$$

$$G_{32}(\rho) = C_0 \rho^3. \tag{6.120}$$

Therefore, the corresponding expressions for $F_{nl}(\rho)$ are as follows:

$$F_{10}(\rho) = C_0 e^{-\rho/2}, \tag{6.121}$$

$$F_{20}(\rho) = C_0 \left(1 - \frac{\rho}{4}\right) e^{-\rho/4}, \tag{6.122}$$

$$F_{21}(\rho) = C_0 \rho e^{-\rho/4}, \tag{6.123}$$

$$F_{30}(\rho) = C_0 \left(1 - \frac{1}{3}\rho + \frac{1}{54}\rho^2\right) e^{-\rho/6}, \tag{6.124}$$

$$F_{31}(\rho) = C_0 \rho \left(1 - \frac{1}{12}\rho\right) e^{-\rho/6}, \tag{6.125}$$

$$F_{32}(\rho) = C_0 \rho^2 e^{-\rho/6}. \tag{6.126}$$

Note that $\rho = 2r/a$ in above equations. Using an appropriate value of C_0 for each case that makes the resulting radial wavefunction normalized, we obtain the results listed in Table 6.1.

Exercise Problems with Solutions

6.1 Calculate the first three transition energies (in the units of cm^{-1}) for Lyman, Balmer, and Paschen like series for the He^+ ion.

Solution 6.1 The reduced mass for electron in helium is

$$\mu = \frac{m_N m_e}{m_N + m_e} = \frac{4.002603254}{4.002603254 + 0.00054854} m_e = 0.999863 m_e.$$

The nuclear charge of He^+ is equal to 2. Therefore, the energy level of electron in He^+ is given by

$$E_n = -4R_{He^+}\frac{1}{n^2}, \qquad n = 1, 2, \cdots$$

where $R_{He^+} = 0.99863 \times 1.0974 \times 10^5\ \text{cm}^{-1} = 1.0972 \times 10^5\ \text{cm}^{-1}$. Thus, the three Lyman series, which correspond to transitions from $n > 1$ to $n = 1$, are as follows:

$$4R_{He^+}\left(1 - \frac{1}{4}\right) = 3.2916 \times 10^5\ \text{cm}^{-1},$$

$$4R_{He^+}\left(1 - \frac{1}{9}\right) = 3.9012 \times 10^5\ \text{cm}^{-1},$$

$$4R_{He^+}\left(1 - \frac{1}{16}\right) = 4.1144 \times 10^5\ \text{cm}^{-1}.$$

Next, the Balmer series, which correspond to transitions from $n > 2$ to $n = 2$, are as follows:

$$4R_{He^+}\left(\frac{1}{4} - \frac{1}{9}\right) = 6.0956 \times 10^4\ \text{cm}^{-1},$$

$$4R_{He^+}\left(\frac{1}{4} - \frac{1}{16}\right) = 8.2292 \times 10^4\ \text{cm}^{-1},$$

$$4R_{He^+}\left(\frac{1}{4} - \frac{1}{25}\right) = 9.2164 \times 10^4\ \text{cm}^{-1}.$$

Finally, the Paschen series, which correspond to transitions from $n > 3$ to $n = 3$, are as follows:

$$4R_{He^+}\left(\frac{1}{9}-\frac{1}{16}\right) = 2.1334 \times 10^4\ \text{cm}^{-1},$$

$$4R_{He^+}\left(\frac{1}{9}-\frac{1}{25}\right) = 3.1209 \times 10^4\ \text{cm}^{-1},$$

$$4R_{He^+}\left(\frac{1}{9}-\frac{1}{36}\right) = 3.6573 \times 10^4\ \text{cm}^{-1}.$$

6.2 Prove that $R_{20}(r)$ and $R_{21}(r)$ in Table 6.1 are solutions satisfying the differential equation, Eq. (6.28). You do not need to include the normalization constant in proving this.

Solution 6.2 Let us use $\rho = 2r/a$. Then, without including the normalization factor,

$$R_{20}(r) = \left(2-\frac{r}{a}\right)e^{-r/(2a)} = \left(2-\frac{\rho}{2}\right)e^{-\rho/4},$$

$$R_{21}(r) = \frac{r}{a}e^{-r/(2a)} = \rho e^{-\rho/4}.$$

The fact that $R_{20}(r)$ is the solution of the radial equation is proved as follows.

$$\frac{d^2}{d\rho^2}\left(\rho(2-\rho)e^{-\rho/4}\right) + \left(-\frac{1}{16}+\frac{1}{\rho}\right)\rho\left(2-\frac{\rho}{2}\right)e^{-\rho/4}$$

$$= \frac{d}{d\rho}\left\{(2-\rho)e^{-\rho/4} - \frac{1}{4}\left(2\rho-\frac{\rho^2}{2}\right)e^{-\rho/4}\right\}$$

$$+ \left(-\frac{1}{16}+\frac{1}{\rho}\right)\rho\left(2-\frac{\rho}{2}\right)e^{-\rho/4}$$

$$= \left\{-1-\frac{1}{4}(2-\rho)-\frac{1}{4}(2-\rho)+\frac{1}{16}\left(2\rho-\frac{\rho^2}{2}\right)\right\}e^{-\rho/4}$$

$$+ \left\{-\frac{1}{16}\left(2\rho-\frac{\rho^2}{2}\right)+\left(2-\frac{\rho}{2}\right)\right\}e^{-\rho/4} = 0.$$

The fact that $R_{21}(r)$ is the solution of the radial equation is proved as follows.

$$\frac{d^2}{d\rho^2}\left(\rho^2 e^{-\rho/4}\right)+\left(-\frac{1}{16}+\frac{1}{\rho}-\frac{2}{\rho^2}\right)\left(\rho^2 e^{-\rho/4}\right)$$
$$=\frac{d}{d\rho}\left\{2\rho e^{-\rho/4}-\frac{\rho^2}{4}e^{-\rho/4}\right\}+\left(-\frac{1}{16}+\frac{1}{\rho}-\frac{2}{\rho^2}\right)\left(\rho^2 e^{-\rho/4}\right)$$
$$=\left\{2-\frac{\rho}{2}-\frac{\rho}{2}+\frac{\rho^2}{16}-\frac{\rho^2}{16}+\rho-2\right\}e^{-\rho/4}=0.$$

6.3 Prove that $R_{20}(r)$ and $R_{21}(r)$ in Table 6.1 are not orthogonal to each other. You do not need to include the normalization constant in proving this.

Solution 6.3 This can be shown by direct integration as follows.

$$\int_0^\infty drr^2 R_{20}(r)R_{21}(r)=C\int_0^\infty drr^2\left(2-\frac{r}{a}\right)e^{-r/(2a)}\frac{r}{a}e^{-r/(2a)}$$
$$=\frac{C}{a}\int_0^\infty dr\left(2r^3-\frac{r^4}{a}\right)e^{-r/a}$$
$$=C(\frac{2}{a}3!a^4-\frac{1}{a^2}4!a^5)=-12Ca^3,$$

where C is a nonzero constant that comes from the normalization factors of radial functions. Since this is non-zero, the above shows that $R_{20}(r)$ and $R_{21}(r)$ are non-orthogonal.

6.4 For the radial wavefunction $R_{32}(r)$ in Table 6.1, determine the most probable value of r, and the average potential energy.

Solution 6.4 The radial probability density for this radial wavefunction is as follows:

$$P_{32}(r)=r^2[R_{32}(r)]^2=Nr^2\cdot r^4 e^{-2r/(3a)},$$

where $N=8/(5\cdot 3^6 a^7)$. Taking derivative of $P_{32}(r)$ with respect to r,

$$\frac{d}{dr}P_{32}(r)=N\cdot 6r^5 e^{-2r/(3a)}-Nr^6 e^{-2t/(3a)}\left(-\frac{2}{3a}\right)$$
$$=N\left(6-\frac{2}{3a}r\right)e^{-2r/(3a)}r^5=0.$$

The above equation is satisfied for $r = 9a_0$. The average potential energy is calculated as follows:

$$
\begin{aligned}
\langle V(r)\rangle_{32} &= \int_0^{\infty} dr\, P_{32}(r)\left(-\frac{e^2}{4\pi\epsilon_0 r}\right) \\
&= -\frac{e^2}{4\pi\epsilon_0}\left(\frac{4}{27\sqrt{10}}\right)^2\left(\frac{1}{27a^7}\right)\int_0^{\infty} dr r^5 e^{-2r/(3a)} \\
&= -\frac{e}{4\pi\epsilon_0}\left(\frac{4}{27\sqrt{10}}\right)^2\left(\frac{1}{27a^7}\right)5!\left(\frac{3a}{2}\right)^6 \\
&= -\frac{e}{4\pi\epsilon_0}\frac{1}{9a}.
\end{aligned}
$$

6.5 For an isolated hydrogen atom in space, the average distance of its electron from the nucleus is known to be 1 mm. Then, what is the range of possible values of its energy?

Solution 6.5 Let us first calculate the range of average distance for a given principal quantum number n employing Eq. (6.38). If $l = 0$,

$$\langle r\rangle_{n00} = \frac{3}{2}an^2.$$

For $l = n - 1$,

$$\langle r\rangle_{nn-1m_l} = a\left(\frac{3}{2}n^2 - n^2 + n\right) = a\left(\frac{1}{2}n^2 + n\right).$$

Thus, if we assume that $l = 0$, the average distance of 1 mm corresponds to the following minimum principal quantum number:

$$n_{min} = \left(\frac{2}{3}\frac{1\times 10^{-3}}{5.29\times 10^{-11}}\right)^{1/2} \approx 3550.$$

For this,

$$E_{min} = -\frac{1.0968\times 10^5}{(3550)^2}\ \text{cm}^{-1} = -8.703\times 10^{-3}\ \text{cm}^{-1}.$$

On the other hand, if we assume that $l = n - 1$, the average distance of 1 mm, the maximum principal quantum number is the solution of the following quadratic equation:

$$\frac{1}{2}n^2 + n = \frac{1\times 10^{-3}}{5.29\times 10^{-11}}.$$

Solving this quadratic equation, we find that $n_{max} \approx 6148$. For this,

$$E_{max} = -\frac{1.0968 \times 10^5}{(6148)^2}\ \text{cm}^{-1} = -2.902 \times 10^{-3}\ \text{cm}^{-1}.$$

Thus, the range of energies is -8.703×10^{-3} cm^{-1} $\sim$ -2.902×10^{-3} cm^{-1} or -1.079×10^{-6} eV $\sim$ -3.598×10^{-7} eV.

6.6 Prove that p_x orbital is an eigenfunction of $\hat{L}_x$ and determine its eigenvalue.

Solution 6.6 This can be shown by applying $\hat{L}_x$ (in position representation) directly to p_x (with normalization constant omitted) as follows:

$$\begin{aligned}\hat{L}_x p_x &= i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)\sin\theta\cos\phi \\ &= i\hbar\left(\sin\phi\cos\theta\cos\phi + \cot\theta\cos\phi\sin\theta(-\sin\phi)\right) \\ &= i\hbar\left(\cos\theta\sin\phi\cos\phi - \cos\theta\cos\phi\sin\phi\right) = 0 = 0p_x.\end{aligned}$$

This proves that p_x is an eigenfunction of $\hat{L}_x$ with eigenvalue 0.

6.7 Prove that d_{xz} orbital is not an eigenfunction of $\hat{L}_z$.

Solution 6.7 Let us apply $\hat{L}_z$ to d_{xz} orbital (with normalization constant omitted) as follows:

$$\frac{\hbar}{i}\frac{\partial}{\partial\phi}\sin\theta\cos\theta\cos\phi = -\frac{\hbar}{i}\sin\theta\cos\theta\sin\phi.$$

The final expression in the above expression is not proportional to d_{xz}. Therefore, this is not an eigenfunction of $\hat{L}_z$.

6.8 For two electrons 1 and 2 with $L_1 = 0$ and $L_2 = 1$, respectively, list all possible values of L, S, and J, and write all the electronic terms representing states possible for this system of two electrons.

Solution 6.8 The resulting values of L and S are as follows: $L = 1$, $S = 0, 1$. For these values of L and S, $J = 0, 1, 2$. The resulting terms are as follows: $^3\text{P}_0$, $^3\text{P}_1$, $^3\text{P}_2$, $^1\text{P}_1$.

6.9 For two electrons 1 and 2 with $L_1 = 1$ and $L_2 = 1$, respectively, list all possible values of L, S, and J, and write all the electronic terms representing states possible for this system of two electrons.

Solution 6.9 Possible values of L and S, and the corresponding values of J and terms are shown in the table below.

L	S	J	Terms
0	0	0	$^1S_0$
0	1	1	$^3S_1$
1	0	1	$^1P_1$
1	1	0, 1, 2	$^3P_0, {}^3P_1, {}^3P_2$
2	0	2	$^1D_2$
2	1	1, 2, 3	$^3D_1, {}^3D_2, {}^3D_3$

6.10 For two electrons 1 and 2 with $L_1 = 2$ and $L_2 = 3$, respectively, list all possible values of L, S, and J, and write all the electronic terms representing states possible for this system of two electrons.

Solution 6.10 Possible values of L and S, and the corresponding values of J and terms are shown in the table below.

L	S	J	Terms
1	0	1	$^1P_1$
1	1	0, 1, 2	$^3P_0, {}^3P_1, {}^3P_2$
2	0	2	$^1D_2$
2	1	1, 2, 3	$^3D_1, {}^3D_2, {}^3D_3$
3	0	3	$^1F_3$
3	1	2, 3, 4	$^3F_2, {}^3F_3, {}^3F_4$
4	0	4	$^1G_4$
4	1	3, 4, 5	$^3G_3, {}^3G_4, {}^3G_5$
5	0	5	$^1H_5$
5	1	4, 5, 6	$^3H_4, {}^3H_5, {}^3H_6$

Problems

6.11 Calculate the first three transition energies (in the units of cm^{-1}) for Lyman, Balmer, and Paschen like series for the Li^{2+} ion.

6.12 For the radial wavefunction $R_{31}(r)$ in Table 6.1, determine the most probable value of r, and the average potential energy.

6.13 The electron of a hydrogen atom is in a state with principal quantum number $n = 2$ and angular momentum quantum number $l = 1$. Calculate its average kinetic and potential energies.

6.14 For all the radial functions listed in Table 6.1, confirm Eqs. (6.37) and (6.38).

6.15 For all the radial functions listed in Table 6.1, calculate $\langle \Delta \hat{r} \rangle = \langle \hat{r}^2 \rangle - \langle \hat{r} \rangle^2$.

6.16 An electron in a hydrogen atom is in a state represented by the following wavefunction: $\psi(\mathbf{r}) = C\left(2e^{-r/a_0} + (r/a_0)e^{-r/(2a_0)}\right)$. This is not an eigenstate of the Hamiltonian. Explain why and calculate the expectation value of the energy?

6.17 The electron in a hydrogen atom is in a state represented by the following wavefunction:

$$\psi(r, \theta, \phi) = \frac{1}{\sqrt{24\pi}} \left(\frac{1}{2a}\right)^{3/2} \left(2 + (\sqrt{3}\sin\theta\cos\phi - 1)\frac{r}{a}\right) e^{-r/(2a)}.$$

(a) Prove that this is an eigenstate of the Hamiltonian and determine its eigenvalue.
(b) Prove that this is not an eigenstate of $\hat{L}^2$ and determine its expectation value.

6.18 For two electrons 1 and 2 with $L_1 = 1$ and $L_2 = 3$, respectively, list all possible values of L, S, and J, and write all the electronic terms representing states possible for this system of two electrons.

6.19 For two electrons 1 and 2 with $L_1 = 2$ and $L_2 = 2$, respectively, list all possible values of L, S, and J, and write all the electronic terms representing states possible for this system of two electrons.

Chapter 7
Approximation Methods for Time Independent Schrödinger Equation



The simplicities of natural laws arise through the complexities of the language we use for their expression.

— Eugene Wigner

Abstract This chapter is focused on two standard methods of approximating the solution of a time independent Schrödinger equation, the variational principle and the time independent perturbation theory. The variational principle states that the true ground state energy of a quantum system is always smaller than any approximation, for which a simple quantum mechanical proof is provided. Then, assuming a trial state given by a a linear combination of predetermined basis states, which are not necessarily orthogonal, an eigenvalue equation for the coefficients of the linear combination and the energy is derived. Solution of this equation results in the best choice of the linear combination and the corresponding variational approximation for the ground state energy. The perturbation theory is applicable for the case where the Hamiltonian of a system is the sum of a zeroth order Hamiltonian term with known solutions and a small perturbation term. First, for the case where there is no degeneracy in the zeroth order Hamiltonian, general expressions for the first and second order corrections for both energies and states are derived. Then, for the case where the zeroth order Hamiltonian is degenerate, corrections of the energy up to the second order and of the state up to the first order of the perturbation are derived.

Analytic solutions for the time independent Schrödinger equation exist only for very few systems. For most cases, one has to resort to either approximation methods or numerical solutions. The variational principle and the time independent perturbation theory serve as two major methods for such approximation. The objective of this chapter is to explain the theoretical bases of these approximation methods and derive important expressions that can be employed for actual applications.

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7.1 Variational Principle

The variational principle provides a general strategy of approximation for a broad range of problems. It has long been used widely for solving any kind of eigenvalue or optimization problems for the cases where the quantity of interest is bounded. The idea behind the variational principle is simple. Let us consider any mathematical operator $\hat{O}$ defined with respect to a certain set of functions, S_f, and that one can identify a set of normalized and orthogonal eigenfunctions $\phi_n(x)$'s such that any function in S_f can be determined as a unique linear combination of $\phi_n(x)$'s. In other words, let us assume that there is a unique expression for any function $f(x)$ in S_f as follows:

$$f(x) = C_1\phi_1(x) + C_2\phi_2(x) + \cdots + C_k\phi_k(x) + \cdots . \tag{7.1}$$

Then,

$$\int dx f^*(x)\hat{O}f(x) = |C_1|^2\lambda_1 + |C_2|^2\lambda_2 + \cdots + |C_k|^2\lambda_k + \cdots , \tag{7.2}$$

where λ_k is an eigenvalue for $\phi_k(x)$ such that $\hat{O}\phi_k(x) = \lambda_k\phi_k(x)$ and the fact that $\int dx\phi_k^*(x)\phi_j(x) = \delta_{kj}$ has been used. In case all λ_k's are real valued and bounded from below (or above), it is clear that Eq. (7.2) divided by a proper normalization constant should also be bounded the same way. Although functions depending on only one variable x were considered above, the same principle holds for any function that depends on multiple variables. The Hamiltonian operator in quantum mechanics has all the properties validating these assumptions, which can be utilized for finding approximations in case exact solutions are difficult to find.

7.1.1 General Case

The most common use of the variational principle in quantum mechanics is finding out the approximation for the ground state energy. The underlying theorem, employing the Dirac notation, can be stated as follows.

Theorem 7.1 *Consider a system represented by a Hamiltonian operator $\hat{H}$, which is Hermitian. The expectation value of the Hamiltonian for any state $|\phi\rangle$, which is not necessarily normalized, is always bounded from below by its true ground state energy E_g as follows:*

$$E_\phi = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle} \geq E_g. \tag{7.3}$$

Proof Let us denote the complete set of eigenstates of $\hat{H}$ as $|\psi_k\rangle$'s, which are normalized. Thus, any state can be represented in terms of linear combination of these states as follows:

$$|\phi\rangle = \sum_k a_k |\psi_k\rangle, \tag{7.4}$$

and its norm is given by the sum of absolute squares of a_k's as follows:

$$\langle\phi|\phi\rangle = \sum_k \sum_{k'} a_k a_{k'}^* \langle\psi_{k'}|\psi_k\rangle = \sum_k \sum_{k'} a_k a_{k'}^* \delta_{kk'} = \sum_k |a_k|^2. \tag{7.5}$$

On the other hand,

$$\langle\phi|\hat{H}|\phi\rangle = \sum_k \sum_{k'} a_k a_{k'}^* \langle\psi_{k'}|\hat{H}|\psi_k\rangle = \sum_k \sum_{k'} a_k a_{k'}^* E_k \delta_{kk'} = \sum_k |a_k|^2 E_k. \tag{7.6}$$

Then, E_ϕ defined by Eq. (7.3) can be calculated as follows:

$$E_\phi = \frac{\sum_k |a_k|^2 E_k}{\sum_k |a_k|^2} = \frac{E_g \sum_k |a_k|^2 + \sum_k (E_k - E_g)|a_k|^2}{\sum_k |a_k|^2}. \tag{7.7}$$

In the second equality of the above expression, the fact that $E_k = E_g + (E_k - E_g)$ was used. Now splitting the numerator into two terms, we find that

$$E_\phi = E_g + \frac{\sum_k (E_k - E_g)|a_k|^2}{\sum_k |a_k|^2} \geq E_g, \tag{7.8}$$

where the fact that $E_k - E_g \geq 0$, which should be satisfied because no eigenvalue can be lower than the ground state eigenvalue, has been used. The above equation completes the proof of the variational principle. □

The power of the variational principle is the boundedness of E_ϕ. This guarantees that any effort to lower E_ϕ always results in a better approximation for the true ground state energy. It is often the case that the variational principle sometimes serves as the last reliable resort in quantum mechanics when finding good enough approximations for solutions are extremely difficult. The fact that the choice of the state $|\phi\rangle$, which is called a trial state, can be chosen without any restriction is also a great advantage. However, in practice, it is impossible to search for all possible states. Rather, the search is limited to a class of states that can be represented by a set of known basis states.

7.1.2 Variational Principle for Trial States as Linear Combinations of Basis States

One systematic and mathematically well understood way to construct a trial state is to express it as a set of linearly independent states: $|f_1\rangle, \ldots, |f_n\rangle$. While these are independent states, we do not necessarily have to assume that they are orthogonal, which significantly expands the choice of basis states one can make. Thus, let us assume that the trial state is given by

$$|\phi\rangle = C_1|f_1\rangle + C_2|f_2\rangle + \cdots + C_n|f_n\rangle, \tag{7.9}$$

where $C_1, \ldots, C_n$ are unknown constants. The components of a given Hamiltonian with respect to these states are denoted as

$$H_{jk} = \langle f_j|\hat{H}|f_k\rangle, \tag{7.10}$$

and the overlap matrix elements of the basis states are given by

$$S_{jk} = \langle f_j|f_k\rangle. \tag{7.11}$$

Then, the statement of the variational principle for the present case reduces to the following inequality:

$$E_\phi = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{\sum_j \sum_k C_j^* C_k H_{jk}}{\sum_j \sum_k C_j^* C_k S_{jk}} \geq E_g. \tag{7.12}$$

The best approximation of E_ϕ for E_g can be found by choosing C_k's minimizing E_ϕ given above. A necessary condition for this is that the partial derivative of E_ϕ with respect to C_k's and C_k^*'s, which can be viewed as independent complex variables, should be zero. Thus, first taking the partial derivative of E_ϕ with respect to one coefficient, for example, for C_i, where i can be any of the indices,

$$\begin{aligned}\frac{\partial E_\phi}{\partial C_i} &= \frac{\sum_j C_j^* H_{ji}}{\sum_j \sum_k C_j^* C_k S_{jk}} - \frac{\sum_j \sum_k C_j^* C_k H_{jk} \left(\sum_{j'} C_{j'}^* S_{j'i}\right)}{(\sum_j \sum_k C_j^* C_k S_{jk})^2} \\ &= \frac{\sum_{j=1}^n \left(H_{ji} C_j^* - E_\phi C_j^* S_{ji}\right)}{\sum_j \sum_k C_j^* C_k S_{jk}} = 0\ ,\ i = 1, \ldots, n,\end{aligned} \tag{7.13}$$

where Eq. (7.12) has been used in the second equality.

Note that the denominator in Eq. (7.13) is nonzero and that it is satisfied as long as the numerator becomes zero. Since $H_{ji} = H_{ij}^*$ and $S_{ji} = S_{ij}^*$, it is thus equivalent to the following identity:

$$\sum_{j=1}^{n} \left(H_{ij}^* C_j^* - E_\phi S_{ij}^* C_j^* \right) = 0,\ i = 1, \ldots, n. \tag{7.14}$$

Similarly, taking the partial derivative of E_ϕ given by Eq. (7.12) with respect to C_i^*,

$$\begin{aligned} \frac{\partial E_\phi}{\partial C_i^*} &= \frac{\sum_j C_j H_{ij}}{\sum_j \sum_k C_j^* C_k S_{jk}} - \frac{\sum_j \sum_k C_j^* C_k H_{jk} \left(\sum_{k'} C_{k'} S_{ik'} \right)}{\left(\sum_j \sum_k C_j^* C_k S_{jk} \right)^2} \\ &= \frac{\sum_{j=1}^{n} \left(H_{ij} C_j - E_\phi S_{ij} C_j \right)}{\sum_j \sum_k C_j^* C_k S_{jk}} = 0\ ,\ i = 1, \ldots, n. \end{aligned} \tag{7.15}$$

This equation is satisfied if the numerator is zero, and is thus equivalent to the following equation:

$$\sum_{j=1}^{n} \left(H_{ij} C_j - E_\phi S_{ij} C_j \right) = 0,\ i = 1, \ldots, n. \tag{7.16}$$

Note that Eqs. (7.14) and (7.16) are complex conjugates of each other. For convenience, the latter is used in general.

Variational Principle for Linear Combination of Basis States

Equation (7.16), after dropping the subscript in E_ϕ, is expressed as

$$\sum_{j=1}^{n} \left(H_{ij} - E S_{ij} \right) C_j = 0,\ ,i = 1, \cdots, n, \tag{7.17}$$

which is a general linear equation to be solved for E and C_j's. In a matrix notation, the above equation can also be expressed as

$$\begin{pmatrix} H_{11} - E S_{11} & H_{12} - E S_{12} & \ldots & H_{1n} - E S_{1n} \\ H_{21} - E S_{21} & H_{22} - E S_{22} & \ldots & H_{2n} - E S_{2n} \\ \ldots & \ldots & \ldots & \ldots \\ H_{n1} - E S_{n1} & \ldots & H_{nn-1} - E S_{nn-1} & H_{nn} - E S_{nn} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ \vdots \\ C_n \end{pmatrix} = 0. \tag{7.18}$$

(continued)

For the solution of the above equation to exist for nonzero C_j's, it is necessary for the following determinant to be zero.

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \dots & H_{2n} - ES_{2n} \\ \dots & \dots & \dots & \dots \\ H_{n1} - ES_{n1} & \dots & H_{nn-1} - ES_{nn-1} & H_{nn} - ES_{nn} \end{vmatrix} = 0. \tag{7.19}$$

The above equation is called *secular equation*. Solving this secular equation, one can find n solutions for E. Inserting each value of E into Eq. (7.18) and also using the normalization condition, one can find the set of C_j's corresponding to each solution of E. This completes the solution of Eq. (7.18). The lowest eigenvalue and the corresponding eigenstate are deemed as the best approximations for the ground state energy and the ground eigenstate.

It is possible [2] to show that all the eigenstates of Eq. (7.18) are orthogonal as is explained below. Let us denote the αth eigenvalue as E_α and assume that there exists a unique set of coefficients $C_j^{(\alpha)}$'s such that

$$\sum_{j=1}^{n} (H_{ij} - E_\alpha S_{ij}) C_j^{(\alpha)} = 0, \; i = 1, \cdots, n. \tag{7.20}$$

Then, we can define the αth eigenstate as follows:

$$|\phi_\alpha\rangle = \sum_{j=1}^{n} C_j^{(\alpha)} |f_j\rangle. \tag{7.21}$$

Theorem 7.2 *Two states $|\phi_\alpha\rangle$ and $|\phi_\beta\rangle$ defined by Eq. (7.21) with coefficients satisfying Eq. (7.20) for two different energies $E_\alpha \neq E_\beta$ are orthogonal to each other.*

Proof First, let us consider the following matrix elements:

$$\langle f_i | \hat{H} | \phi_\alpha \rangle = \sum_{j=1}^{n} C_j^{(\alpha)} \langle f_i | \hat{H} | f_j \rangle = \sum_{j=1}^{n} H_{ij} C_j^{(\alpha)}, \tag{7.22}$$

$$\langle f_i | \phi_\alpha \rangle = \sum_{j=1}^{n} C_j^{(\alpha)} \langle f_i | f_j \rangle = \sum_{j=1}^{n} C_j^{(\alpha)} S_{ij}. \tag{7.23}$$

Multiplying Eq. (7.23) with E_α, we find that

$$E_\alpha \langle f_i | \phi_\alpha \rangle = \sum_{j=1}^{n} E_\alpha C_j^{(\alpha)} S_{ij}. \tag{7.24}$$

Combining Eqs. (7.22) and (7.24), we find that Eq. (7.20) can be expressed as

$$\langle f_i | (\hat{H} - E_\alpha) | \phi_\alpha \rangle = 0, \; i = 1, \cdots, n \tag{7.25}$$

Now consider another eigenstate $|\phi_\beta\rangle = C_j^{(\beta)} |f_j\rangle$, where $E_\beta \neq E_\alpha$. Then, using the above identity, it is straightforward to show that

$$\langle \phi_\beta | (\hat{H} - E_\alpha) | \phi_\alpha \rangle = \sum_{j=1}^{n} C_j^{(\beta)*} \langle f_j | (\hat{H} - E_\alpha) | \phi_\alpha \rangle = 0. \tag{7.26}$$

In a similar manner, or exchanging α and β, one can also show that

$$\langle \phi_\alpha | (\hat{H} - E_\beta) | \phi_\beta \rangle = 0. \tag{7.27}$$

Subtracting the complex conjugate of Eq. (7.27) from Eq. (7.26) and noting the fact that E_α and E_β are real valued numbers, we then find that

$$(E_\alpha - E_\beta) \langle \phi_\alpha | \phi_\beta \rangle = 0. \tag{7.28}$$

For $E_\alpha \neq E_\beta$, the above equation proves that $\langle \phi_\alpha | \phi_\beta \rangle = \langle \phi_\beta | \phi_\alpha \rangle = 0$. □

As is clear from the above proof, in case $E_\alpha = E_\beta$, the two states $|\phi_\alpha\rangle$ and $|\phi_\beta\rangle$ do not have to be orthogonal to each other. However, even in such case, it is still possible to find out two orthogonal states out of the linear combination of those states. In this way, it is possible to find a set of orthogonal states satisfying the variational principle.

As a simple example, consider a trial state as a linear combination of two basis states as follows: $|\phi\rangle = C_1 |f_1\rangle + C_2 |f_2\rangle$. In addition, let us assumed that $|f_1\rangle$ and $|f_2\rangle$ are normalized. All the matrix elements are assumed to be real numbers, and $H_{11} = H_{22} = H_d$ and $H_{12} = H_{21} = H_c$. Then,

$$\begin{pmatrix} H_d - E & H_c - ES \\ H_c - ES & H_d - E \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0, \tag{7.29}$$

where $S = \langle f_1 | f_2 \rangle = \langle f_2 | f_1 \rangle$. For the above equation to be satisfied for nonzero values of C_1 and C_2,

$$\begin{vmatrix} H_d - E & H_c - ES \\ H_c - ES & H_d - E \end{vmatrix} = 0, \tag{7.30}$$

which is equivalent to the following quadratic equation:

$$(H_d - E)^2 - (H_c - ES)^2 = (H_d - E + H_c - ES)(H_d - E - H_c + ES) = 0. \tag{7.31}$$

The two solutions of the above equation are as follows:

$$E_+ = \frac{H_d + H_c}{1 + S}, \tag{7.32}$$

$$E_- = \frac{H_d - H_c}{1 - S}. \tag{7.33}$$

The eigenstates corresponding to the above two eigenvalues can be found by using each eigenvalue in Eq. (7.18) and solving the linear equation with respect to C_1 and C_2 and employing the normalization condition. The resulting expressions for the eigenstates are as follows:

$$|\phi_+\rangle = \frac{1}{\sqrt{2(1+S)}}\left(|f_1\rangle + |f_2\rangle\right), \tag{7.34}$$

$$|\phi_-\rangle = \frac{1}{\sqrt{2(1-S)}}\left(|f_1\rangle - |f_2\rangle\right). \tag{7.35}$$

7.2 Time Independent Perturbation Theory

Perturbation theory is a general approximation method for solving a differential or integral equation, and plays an important role in practical applications of quantum mechanics because there are only few limited cases for which exact solutions of the Schrödinger equation are available. The term perturbation refers to a small deviation or disturbance from the original equation, and the theory allows finding approximate solutions in a systematic manner on the basis of solutions for the original unperturbed equation. Perturbation theory can be developed for both time independent and time dependent Schrödinger equations. The former, known as time independent perturbation theory, is presented here whereas the latter, known as time dependent perturbation theory, will be introduced in Chap. 10.

The idea of time independent perturbation theory can be summarized in a general way for any eigenvalue problem. Let us consider a zeroth order operator $\hat{O}^{(0)}$ and its eigenfunction or vector $f^{(0)}$ with eigenvalue $\lambda^{(0)}$ as follows.

$$\hat{O}^{(0)} f^{(0)} = \lambda^{(0)} f^{(0)}. \tag{7.36}$$

Then, given that the operator is perturbed by an additional perturbation operator $\hat{O}^{(1)}$, the main question is what will be the resulting corrections for $f^{(0)}$ and $\lambda^{(0)}$. To find the answer for this question, it is useful to introduce a small parameter ϵ

that controls the magnitude of the perturbation and try to find out the solution for $\hat{O}(\epsilon) = \hat{O}^{(0)} + \epsilon\hat{O}^{(1)}$ as power series with respect to ϵ. In other words, let us assume that

$$f(\epsilon) = f^{(0)} + \epsilon f^{(1)} + \epsilon^2 f^{(2)} + \cdots , \tag{7.37}$$

$$\lambda(\epsilon) = \lambda^{(0)} + \epsilon\lambda^{(1)} + \epsilon^2\lambda^{(2)} + \cdots . \tag{7.38}$$

Then, employing these expressions in the new eigenvalue equation, $\hat{O}(\epsilon)f(\epsilon) = \lambda(\epsilon)f(\epsilon)$ and expanding the resulting expression with respect to ϵ on both sides, we obtain the following equation:

$$\begin{aligned}
&\left(\hat{O}^{(0)} + \epsilon\hat{O}^{(1)}\right)\left(f^{(0)} + \epsilon f^{(1)} + \epsilon^2 f^{(2)} + \cdots\right) \\
&= \hat{O}^{(0)} f^{(0)} + \epsilon\left(\hat{O}^{(0)} f^{(1)} + \hat{O}^{(1)} f^{(0)}\right) + \epsilon^2\left(\hat{O}^{(0)} f^{(2)} + \hat{O}^{(1)} f^{(1)}\right) + \cdots \\
&= \lambda^{(0)} f^{(0)} + \epsilon\left(\lambda^{(0)} f^{(1)} + \lambda^{(1)} f^{(0)}\right) \\
&\quad + \epsilon^2\left(\lambda^{(0)} f^{(2)} + \lambda^{(1)} f^{(1)} + \lambda^{(2)} f^{(0)}\right) + \cdots ,
\end{aligned} \tag{7.39}$$

where both left and right sides of the equation were grouped into terms of the same order of ϵ. At the zeroth order of ϵ, the above equation is already satisfied by construction. In order for the above equation to be satisfied for any value of ϵ including the particular case where $\epsilon = 1$, the equation for each term of ϵ^n with $n = 1, 2, 3, \cdots$ has to be solved. This is a nontrivial task because corrections for both eigenfunction (or eigenvector) and eigenvalue have to be calculated, and solving the equation for the nth order in general requires solutions for all the lower orders. However, outcomes of such a task, once completed, can serve as powerful and general expressions applicable to a wide range of realistic situations.

In applying the perturbation theory for quantum mechanics, it is particularly useful to employ the Dirac notation as described below. Let us first consider a zeroth order Hamiltonian $\hat{H}_0$ for which the eigenstates and the eigenvalues are known, and denote them as $|\psi_n^{(0)}\rangle$'s and $E_n^{(0)}$'s. Here, n is a label representing each eigenstate. Thus, for each n,

$$\hat{H}_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle, \tag{7.40}$$

where $\langle\psi_n^{(0)}|\psi_m^{(0)}\rangle = \delta_{nm}$. Then, let us introduce a perturbation Hamiltonian $\hat{H}_1$, which is assumed[1] to be small compared to $\hat{H}_0$, and consider the following total

[1] The smallness of $\hat{H}_1$ implies that its effect on the change of $E_n^{(0)}$ is small compared to the level spacing of $E_n^{(0)}$'s. Note that this definition of smallness has a problem in case there is degeneracy, for which a separate treatment is needed.

Hamiltonian:

$$\hat{H} = \hat{H}_0 + \epsilon \hat{H}_1, \tag{7.41}$$

where ϵ does not necessarily have to be small and can simply be considered as a parameter to keep track of the order of the perturbation approximation. Once the solution is obtained for each order of ϵ, one can then set $\epsilon = 1$ without losing generality of the solution because it can be viewed that the small parameter has already been absorbed into $\hat{H}_1$.

In short, the perturbation theory amounts to solving the following equation:

$$(\hat{H}_0 + \epsilon \hat{H}_1)|\psi_n\rangle = E_n|\psi_n\rangle, \tag{7.42}$$

by expanding $|\psi_n\rangle$ and E_n as powers of ϵ such that each term in the expansion can ultimately be expressed in terms of $|\psi_n^{(0)}\rangle$ and $E_n^{(0)}$. The development of the perturbation theory differs depending on whether $E_n^{(0)}$'s are degenerate or non-degenerate. The latter case is straightforward, and is described first.

7.2.1 Non-Degenerate Perturbation Theory

The starting point of the perturbation theory is the complete set of $|\psi_n^{(0)}\rangle$'s, which are normalized eigenstates of $\hat{H}_0$, and their respective eigenvalues $E_n^{(0)}$'s. All of these eigenvalues are assumed to be different for the present case. First, let us assume that the eigenstates and eigenvalues of the total Hamiltonian satisfying Eq. (7.42) can be expanded as follows:

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \epsilon|\psi_n^{(1)}\rangle + \epsilon^2|\psi_n^{(2)}\rangle + \ldots, \tag{7.43}$$

$$E_n = E_n^{(0)} + \epsilon E_n^{(1)} + \epsilon^2 E_n^{(2)} + \ldots. \tag{7.44}$$

In Eq. (7.43), the second and the third terms can be expanded in terms of the eigenstates of the zeroth order Hamiltonian as follows:

$$|\psi_n^{(1)}\rangle = \sum_{m\neq n} C_m^{(1)}|\psi_m^{(0)}\rangle, \tag{7.45}$$

$$|\psi_n^{(2)}\rangle = \sum_{m\neq n} C_m^{(2)}|\psi_m^{(0)}\rangle, \tag{7.46}$$

where the summation does not include the index n because it is already represented by the zeroth order state. Including this zeroth order state in the perturbation terms simply amounts to changing the normalization constant of the zeroth order state and does not result in any actual difference.

Employing Eqs. (7.43) and (7.44), the Schrödinger equation for the perturbed Hamiltonian, Eq. (7.42), can be expressed as

$$
\begin{aligned}
&(\hat{H}_0 + \epsilon \hat{H}_1) \left(|\psi_n^{(0)}\rangle + \epsilon |\psi_n^{(1)}\rangle + \epsilon^2 |\psi_n^{(2)}\rangle + \ldots \right) \\
&= (E_n^{(0)} + \epsilon E_n^{(1)} + \epsilon^2 E_n^{(2)} + \ldots) \left(|\psi_n^{(0)}\rangle + \epsilon |\psi_n^{(1)}\rangle + \epsilon^2 |\psi_n^{(2)}\rangle + \ldots \right).
\end{aligned} \tag{7.47}
$$

The perturbation theory amounts to solving the above equation for each order of ϵ as described below. First, for the order of ϵ^0,

$$
\hat{H}_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle, \tag{7.48}
$$

which is already satisfied by the starting assumption, Eq. (7.40). The next order terms are considered below.

First Order Terms of the Perturbation Expansion

The terms corresponding to the first order of ϵ in Eq. (7.47), when combined, lead to the following first order equation:

$$
\hat{H}_1 |\psi_n^{(0)}\rangle + \hat{H}_0 |\psi_n^{(1)}\rangle = E_n^{(1)} |\psi_n^{(0)}\rangle + E_n^{(0)} |\psi_n^{(1)}\rangle, \tag{7.49}
$$

where $E_n^{(1)}$ and $|\psi_n^{(1)}\rangle$ are yet unknown and need to be determined. Note that $|\psi_n^{(1)}\rangle$ is assumed to be given by Eq. (7.45). Thus, determining this amounts to determining all the coefficients, $C_m^{(1)}$'s.

Equation (7.49) can be solved as follows. First, taking inner product with $\langle\psi_n^{(0)}|$, we obtain

$$
\langle\psi_n^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle + \langle\psi_n^{(0)}|\hat{H}_0|\psi_n^{(1)}\rangle = E_n^{(1)}\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle + E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle, \tag{7.50}
$$

where $\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle = 0$. In addition, $\langle\psi_n^{(0)}|\hat{H}_0|\psi_n^{(1)}\rangle = E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle = 0$ because $|\psi_n^{(1)}\rangle$ is expanded with respect to states that are orthogonal to $|\psi_n^{(0)}\rangle$ as can be seen from Eq. (7.45). On the righthand side of the above equation, $\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle = 1$. For these reasons, we obtain a simple expression for the first order perturbation energy as summarized below.

First Order Perturbation Energy

Equation (7.50) simplifies to the following expression for the first order perturbation correction of the energy.

$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle. \tag{7.51}$$

Note that the above expression is nothing but the expectation value of the perturbation Hamiltonian $\hat{H}_1$ with respect to the zeroth order eigenstate.

Next, in order to determine $|\psi_n^{(1)}\rangle$, let us take inner product of Eq. (7.49) with $\langle \psi_m^{(0)}|$, for $m \neq n$. This leads to

$$\langle \psi_m^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle + \langle \psi_m^{(0)} | \hat{H}_0 | \psi_n^{(1)} \rangle = E_n^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle. \tag{7.52}$$

Note that $\langle \psi_m^{(0)} | \hat{H}_0 = \langle \psi_m^{(0)} | E_m^{(0)}$. From the definition of Eq. (7.45), $\langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = C_m^{(1)}$. Therefore, the above equation is equivalent to

$$\langle \psi_m^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle + E_m^{(0)} C_m^{(1)} = E_n^{(0)} C_n^{(1)}, \tag{7.53}$$

This equation can be solved easily for $C_m^{(1)}$ and leads to

$$C_m^{(1)} = \frac{\langle \psi_m^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}. \tag{7.54}$$

The above expression is well-defined for the present case because there is no degeneracy in the zeroth order energies. This also shows why the present approach cannot be used when there is degeneracy.

First Order Perturbation State

Employing the expression for $C_m^{(1)}$ in the definition of Eq. (7.45), we obtain the following first order perturbation correction for the state $|\psi_n^{(0)}\rangle$:

$$|\psi_n^{(1)}\rangle = \sum_{m \neq n} C_m^{(1)} |\psi_m^{(0)}\rangle = \sum_{m \neq n} \frac{|\psi_m^{(0)}\rangle \langle \psi_m^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}. \tag{7.55}$$

Next, let us consider the second order terms of Eq. (7.47) by collecting all the terms that are second order with respect to ϵ.

Second Order Terms of the Perturbation Expansion

The terms corresponding to the second order of ϵ in Eq. (7.47), when combined, result in

$$\hat{H}_1|\psi_n^{(1)}\rangle + \hat{H}_0|\psi_n^{(2)}\rangle = E_n^{(2)}|\psi_n^{(0)}\rangle + E_n^{(1)}|\psi_n^{(1)}\rangle + E_n^{(0)}|\psi_n^{(2)}\rangle, \quad (7.56)$$

where $|\psi_n^{(2)}\rangle$ and $E_n^{(2)}$ are as yet unknown and need to be determined.

Taking inner product of Eq. (7.56) with $\langle\psi_n^{(0)}|$, we obtain

$$\langle\psi_n^{(0)}|\hat{H}_1|\psi_n^{(1)}\rangle + \langle\psi_n^{(0)}|\hat{H}_0|\psi_n^{(2)}\rangle$$
$$= E_n^{(2)}\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle + E_n^{(1)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(2)}\rangle. \quad (7.57)$$

In the lefthand side of the above expression,

$$\langle\psi_n^{(0)}|\hat{H}_0|\psi_n^{(2)}\rangle = E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(2)}\rangle = 0, \quad (7.58)$$

where the second equality comes from the definition of $|\psi_n^{(2)}\rangle$, Eq. (7.46), which is expanded only with respect to those states that are orthogonal to $|\psi_n^{(0)}\rangle$. In addition, in the righthand side of Eq. (7.57), $\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle = 1$, $\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle = 0$, and $\langle\psi_n^{(0)}|\psi_n^{(2)}\rangle = 0$. All of these, when combined, lead to a general expression for the second order perturbation energy as summarized below.

Second Order Perturbation Energy

Equation (7.56) reduces to the following expression for the second order perturbation correction for the energy:

$$E_n^{(2)} = \langle\psi_n^{(0)}|\hat{H}_1|\psi_n^{(1)}\rangle = \sum_{m\neq n} C_m^{(1)}\langle\psi_n^{(0)}|\hat{H}_1|\psi_m^{(0)}\rangle$$
$$= \sum_{m\neq n} \frac{\langle\psi_m^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|\hat{H}_1|\psi_m^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}. \quad (7.59)$$

In each term of the summation in the above expression, the numerator is nonnegative as follows:

$$\langle\psi_m^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|\hat{H}_1|\psi_m^{(0)}\rangle = \left|\langle\psi_m^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle\right|^2 \geq 0. \quad (7.60)$$

(continued)

An important implication of this is that the second order perturbation order correction for the ground state energy always lowers its value because the denominator of each term in the summation is always negative.

We can obtain the second order correction for the state by taking inner product of Eq. (7.56) with $\langle\psi_m^{(0)}|$ for $m \neq n$. Thus, we obtain

$$\langle\psi_m^{(0)}|\hat{H}_1|\psi_n^{(1)}\rangle + \langle\psi_m^{(0)}|\hat{H}_0|\psi_n^{(2)}\rangle = E_n^{(1)}\langle\psi_m^{(0)}|\psi_n^{(1)}\rangle + E_n^{(0)}\langle\psi_m^{(0)}|\psi_n^{(2)}\rangle, \tag{7.61}$$

where the fact that $\langle\psi_m^{(0)}|\psi_n^{(0)}\rangle = 0$ has been used in obtaining the righthand side. Now using Eq. (7.55) and the fact that $\langle\psi_m^{(0)}|\hat{H}_0|\psi_n^{(2)}\rangle = C_m^{(2)}E_m^{(0)}$ on the lefthand side of the above equation, we find that

$$\sum_{m'\neq n} C_{m'}^{(1)}\langle\psi_m^{(0)}|\hat{H}_1|\psi_{m'}^{(0)}\rangle + C_m^{(2)}E_m^{(0)} = E_n^{(1)}C_m^{(1)} + C_m^{(2)}E_n^{(0)}. \tag{7.62}$$

Solving this for $C_m^{(2)}$, we obtain

$$(E_n^{(0)} - E_m^{(0)})C_m^{(2)} = \sum_{m'\neq n} C_{m'}^{(1)}\langle\psi_m^{(0)}|\hat{H}_1|\psi_{m'}^{(0)}\rangle - E_n^{(1)}C_m^{(1)}. \tag{7.63}$$

Employing the expressions for $E_n^{(1)}$ and $C_m^{(1)}$, the above expression can be expressed as

$$C_m^{(2)} = \sum_{m'\neq n} \frac{\langle\psi_m^{(0)}|\hat{H}_1|\psi_{m'}^{(0)}\rangle\langle\psi_{m'}^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle}{(E_n^{(0)} - E_m^{(0)})(E_n^{(0)} - E_{m'}^{(0)})} - \frac{\langle\psi_n^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle\langle\psi_m^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle}{(E_n^{(0)} - E_m^{(0)})^2}. \tag{7.64}$$

Second Order Perturbation State

Employing the expression for $C_m^{(2)}$, Eq. (7.64), in the definition of $|\psi_n^{(2)}\rangle$ given by Eq. (7.46), we obtain the following second order correction for the state $|\psi_n^{(0)}\rangle$:

(continued)

$$|\psi_n^{(2)}\rangle = \sum_{m\neq n} C_m^{(2)}|\psi_m^{(0)}\rangle = \sum_{m\neq n}|\psi_m^{(0)}\rangle\left\{\sum_{m'\neq n}\frac{\langle\psi_m^{(0)}|\hat{H}_1|\psi_{m'}^{(0)}\rangle\langle\psi_{m'}^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle}{(E_n^{(0)}-E_m^{(0)})(E_n^{(0)}-E_{m'}^{(0)})}\right.$$
$$\left. -\frac{\langle\psi_m^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle}{(E_n^{(0)}-E_m^{(0)})^2}\right\}. \quad (7.65)$$

Summarizing all the results obtained above, second order perturbation corrections of energies and states, for the case of $\epsilon = 1$, are

$$E_n = E_n^{(0)} + \langle\psi_n^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle + \sum_{m\neq n}\frac{\langle\psi_m^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|\hat{H}_1|\psi_m^{(0)}\rangle}{E_n^{(0)}-E_m^{(0)}}, \quad (7.66)$$

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \sum_{m\neq n}\frac{|\psi_m^{(0)}\rangle\langle\psi_m^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle}{E_n^{(0)}-E_m^{(0)}}$$
$$+\sum_{m\neq n}|\psi_m^{(0)}\rangle\left\{\sum_{m'\neq n}\frac{\langle\psi_m^{(0)}|\hat{H}_1|\psi_{m'}^{(0)}\rangle\langle\psi_{m'}^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle}{(E_n^{(0)}-E_m^{(0)})(E_n^{(0)}-E_{m'}^{(0)})}\right.$$
$$\left. -\frac{\langle\psi_m^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle}{(E_n^{(0)}-E_m^{(0)})^2}\right\}. \quad (7.67)$$

7.2.2 Degenerate Perturbation Theory

When there is degeneracy, the expressions, Eqs. (7.66) and (7.67), cannot be used because the denominator becomes zero, *i.e.*, $E_n^{(0)} - E_m^{(0)} = 0$, for degenerate states. Thus, a different approach [4–8] should be used for these states.

Let us assume that there are d degenerate eigenstates of $\hat{H}_0$ with energy $E_n^{(0)}$ as shown below:

$$|\psi_{n,1}^{(0)}\rangle, \ldots, |\psi_{n,d}^{(0)}\rangle. \quad (7.68)$$

Then, any linear combination of these states can be an eigenstate with the same energy $E_n^{(0)}$. Among all possible linear combinations, there can be unique d linear combinations that are least affected by the perturbation $\hat{H}_1$ and thus serve as the best starting point for applying the perturbation theory. Let us denote them as $|\phi_{n,k}^{(0)}\rangle$'s with $k = 1, \cdots, d$.

Each $|\phi_{n,k}^{(0)}\rangle$ can be expressed as a linear combination of $|\psi_{n,k}^{(0)}\rangle$'s as follows:

$$|\phi_{n,k}^{(0)}\rangle = C_1|\psi_{n,1}^{(0)}\rangle + \cdots + C_d|\psi_{n,d}^{(0)}\rangle \ , k = 1, \cdots , d. \tag{7.69}$$

Then, let us assume that the eigenstate of $\hat{H}$ that reduces to the one with eigenvalue $E_n^{(0)}$ in the absence of perturbation (the limit of $\epsilon \to 0$), can be expanded as

$$|\phi_{n,k}\rangle = |\phi_{n,k}^{(0)}\rangle + \epsilon|\phi_{n,k}^{(1)}\rangle + \epsilon^2|\phi_{n,k}^{(2)}\rangle + \ldots, \tag{7.70}$$

where detailed expressions for $|\phi_{n,k}^{(1)}\rangle$ and $|\phi_{n,k}^{(2)}\rangle$ will be provided later in this section.

Employing Eq. (7.70) in Eq. (7.42), we obtain

$$\begin{aligned}&(\hat{H}_0 + \epsilon\hat{H}_1)\left(|\phi_{n,k}^{(0)}\rangle + \epsilon|\phi_{n,k}^{(1)}\rangle + \epsilon^2|\phi_{n,k}^{(2)}\rangle + \ldots\right)\\ &= (E_n^{(0)} + \epsilon E_n^{(1)} + \epsilon^2 E_n^{(2)} + \ldots)(|\phi_{n,k}^{(0)}\rangle + \epsilon|\phi_{n,k}^{(1)}\rangle + \epsilon^2|\phi_{n,k}^{(2)}\rangle + \ldots).\end{aligned} \tag{7.71}$$

The zeroth order term (ϵ^0) of Eq. (7.71) is $\hat{H}_0|\phi_{n,k}^{(0)}\rangle = E_n^{(0)}|\phi_{n,k}^{(0)}\rangle$, which is already satisfied since $|\phi_{n,k}^{(0)}\rangle$ is a linear combination of all states with the same energy eigenvalue E_n. The first order terms are considered below.

First Order Term of the Degenerate Perturbation Theory

Collecting all the terms that are first order with respect to ϵ in Eq. (7.71), we obtain

$$\hat{H}_1|\phi_{n,k}^{(0)}\rangle + \hat{H}_0|\phi_{n,k}^{(1)}\rangle = E_n^{(1)}|\phi_{n,k}^{(0)}\rangle + E_n^{(0)}|\phi_{n,k}^{(1)}\rangle. \tag{7.72}$$

Taking inner product of Eq. (7.72) with $\langle\psi_{n,j}^{(0)}|$ for $j = 1, \ldots, d$, we obtain

$$\langle\psi_{n,j}^{(0)}|\hat{H}_1|\phi_{n,k}^{(0)}\rangle + \langle\psi_{n,j}^{(0)}|\hat{H}_0|\phi_{n,k}^{(1)}\rangle = E_{n,k}^{(1)}\langle\psi_{n,j}^{(0)}|\phi_{n,k}^{(0)}\rangle + E_n^{(0)}\langle\psi_{n,j}^{(0)}|\phi_{n,k}^{(1)}\rangle. \tag{7.73}$$

On the lefthand side of the above equation, $\langle\psi_{n,j}^{(0)}|\hat{H}_0|\phi_{n,k}^{(1)}\rangle = E_n^{(0)}\langle\psi_{n,j}^{(0)}|\phi_{n,k}^{(1)}\rangle$, which cancels with the same term on the righthand side. Inserting Eq. (7.69) into the resulting equation leads to a general set of equations that can be solved to determine all the coefficients of Eq. (7.69) as described below.

First Order Correction for the Eigenvalue and the Zeroth Order Correction for the Eigenstate

Employing Eq. (7.69) in Eq. (7.73) and canceling all terms that are identical on both sides of the resulting equation, we obtain

$$H_{1n,j1}C_1 + H_{1n,j2}C_2 + \cdots + H_{1n,jd}C_d = E_n^{(1)}C_j \ , \ j = 1, \ldots, d, \tag{7.74}$$

where

$$H_{1n,jk} = \langle \psi_{n,j}^{(0)} | \hat{H}_1 | \psi_{n,k}^{(0)} \rangle. \tag{7.75}$$

Equation (7.74) for all j can be expressed as the following matrix equation:

$$\begin{pmatrix} H_{1n,11} - E_n^{(1)} & H_{1n,12} & \ldots & H_{1n,1d} \\ H_{1n,21} & H_{1n,22} - E_n^{(1)} & \ldots & H_{1n,2d} \\ & \ldots & & \\ H_{1n,d1} & \ldots & H_{1n,dd-1} & H_{1n,dd} - E_n^{(1)} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ \vdots \\ C_d \end{pmatrix} = 0. \tag{7.76}$$

This matrix equation implies that the following determinant is zero:

$$\begin{vmatrix} H_{1n,11} - E_n^{(1)} & H_{1n,12} & \ldots & H_{1n,1d} \\ H_{1n,21} & H_{1n,22} - E_n^{(1)} & \ldots & H_{1n,2d} \\ & \ldots & & \\ H_{1n,d1} & \ldots & H_{1n,dd-1} & H_{1n,dd} - E_n^{(1)} \end{vmatrix} = 0, \tag{7.77}$$

the solution of which results in the first order degenerate perturbation correction for the energy, $E_{n,k}^{(1)}$ for $k = 1, \cdots, d$.

For each solution of $E_{n,k}^{(1)}$, one can find the corresponding set of coefficients C_k's in Eq. (7.69), which results in the zeroth order eigenstate $|\phi_{n,k}^{(0)}\rangle$ for each $E_{n,k}^{(1)}$ as follows:

$$|\phi_{n,k}^{(0)}\rangle = \sum_{j=1}^{d} C_{n,kj}^{(0)} |\psi_j^{(0)}\rangle, \tag{7.78}$$

where $C_{n,kj}^{(0)}$'s are solutions of the matrix equation, Eq. (7.76), for the eigenvalue $E_{n,k}^{(1)}$ and are assumed to satisfy the normalization condition.

If all the $E^{(1)}_{n,k}$'s are different, one can then apply the non-degenerate perturbation theory employing $|\phi^{(0)}_{n,k}\rangle$'s as the starting point. However, if there is degeneracy in $E^{(1)}_{n,k}$'s, one should again consider linear combination of those degenerate states in going up to the next order in a manner similar to finding the degenerate first order corrections for the eigenvalue and the zeroth order corrections for the states, which results in additional complications.

Here, let us consider only the case where $E^{(1)}_{n,k}$'s are non-degenerate. So far, we have considered the perturbation effects of degenerate states only. However, other non-degenerate states can still make some contributions as well, which have to be added to the results of the degenerate perturbation theory in an appropriate manner.

As the first step for calculating higher order terms, we need to find out the first order correction for the eigenstate $|\phi^{(1)}_{n,k}\rangle$ in Eq. (7.72). Taking inner product of Eq. (7.72) with $\langle\phi^{(0)}_{n,j}|$ for $j \neq k$, we obtain

$$\langle\phi^{(0)}_{n,j}|\hat{H}_1|\phi^{(0)}_{n,k}\rangle + \langle\phi^{(0)}_{n,j}|\hat{H}_0|\phi^{(1)}_{n,k}\rangle = E^{(1)}_n\langle\phi^{(0)}_{n,j}|\phi^{(0)}_{n,k}\rangle + E^{(0)}_n\langle\phi^{(0)}_{n,j}|\phi^{(1)}_{n,k}\rangle. \tag{7.79}$$

In the above equation, $\langle\phi^{(0)}_{n,j}|\hat{H}_1|\phi^{(0)}_{n,k}\rangle = 0$ since $\hat{H}_1$ is diagonal in the basis of new zeroth order eigenstates, $|\phi^{(0)}_{n,j}\rangle$'s. Similarly, $\langle\phi^{(0)}_{n,j}|\phi^{(0)}_{n,k}\rangle = 0$. On the other hand, $\langle\phi^{(0)}_{n,j}|\hat{H}_0|\phi^{(1)}_{n,k}\rangle = E^{(0)}_n\langle\phi^{(0)}_{n,j}|\phi^{(1)}_{n,k}\rangle$, which becomes the same as the second term on the righthand side of the above equation. Thus, Eq. (7.79) is already satisfied.

Therefore, the expansion coefficients of $|\phi^{(1)}_{n,k}\rangle$ with respect to $|\phi^{(0)}_{n,j}\rangle$ remain undetermined at the first order level. On the other hand, the expansion coefficients with respect to other non-degenerates states, $|\psi^{(0)}_m\rangle$, where $m \neq n_1, \cdots, n_d$, can be determined in the same manner as the non-degenerate perturbation theory as summarized below.

First Order Correction for the Degenerate Eigenstate (Incomplete)

Taking inner product of Eq. (7.72) with $\langle\psi^{(0)}_m|$, where $m \neq n$, one can determine the expansion coefficients of $|\phi^{(1)}_{n,k}\rangle$ with respect to $|\psi^{(0)}_m\rangle$'s and find the following expression:

$$|\phi^{(1)}_{n,k}\rangle = \sum_{j\neq k}^{d} D^{(1)}_j|\phi^{(0)}_{n,j}\rangle + \sum_{m\neq n}\sum_{k=1}^{d}\frac{|\psi^{(0)}_m\rangle\langle\psi^{(0)}_m|\hat{H}_1|\phi^{(0)}_{n,k}\rangle}{E^{(0)}_n - E^{(0)}_m}, \tag{7.80}$$

where $D^{(1)}_j$'s are yet undetermined. Consideration of the second order perturbation terms is necessary to determine these as will be shown below.

The second order corrections for the eigenvalue and eigenstate can be obtained by considering all the second order terms in Eq. (7.71) as explained below.

Second Order Term of the Degenerate Perturbation Theory

Collecting all the terms that are second order with respect to ϵ in Eq. (7.71), we obtain

$$\hat{H}_0|\phi_{n,k}^{(2)}\rangle + \hat{H}_1|\phi_{n,k}^{(1)}\rangle = E_n^{(0)}|\phi_{n,k}^{(2)}\rangle + E_{n,k}^{(1)}|\phi_{n,k}^{(1)}\rangle + E_{n,k}^{(2)}|\phi_{n,k}^{(0)}\rangle, \quad (7.81)$$

where $|\phi_{n,k}^{(1)}\rangle$ is orthogonal to $|\phi_{n,k}^{(0)}\rangle$ according to Eq. (7.80) and $|\phi_{n,k}^{(2)}\rangle$ is also assumed to be orthogonal to $|\phi_{n,k}^{(0)}\rangle$ by construction. In the above equation, $E_{n,k}^{(2)}$ and $|\phi_{n,k}^{(2)}\rangle$ as well as part of $|\phi_{n,k}^{(1)}\rangle$ are yet undetermined, for which the equation needs to be solved.

Let us take inner product of Eq. (7.81) with $\langle\phi_{n,k}^{(0)}|$. Then,

$$\langle\phi_{n,k}^{(0)}|\hat{H}_0|\phi_{n,k}^{(2)}\rangle + \langle\phi_{n,k}^{(0)}|\hat{H}_1|\phi_{n,k}^{(1)}\rangle = E_{n,k}^{(2)}, \quad (7.82)$$

where the fact that $|\phi_{n,k}^{(1)}\rangle$ and $|\phi_{n,k}^{(2)}\rangle$ are orthogonal to $|\phi_{n,k}^{(0)}\rangle$ has been used on the righthand side. On the lefthand side of the above equation, the first term also becomes zero as follows: $\langle\phi_{n,k}^{(0)}|\hat{H}_0|\phi_{n,k}^{(2)}\rangle = E_n^{(0)}\langle\phi_{n,k}^{(0)}|\phi_{n,k}^{(2)}\rangle = 0$. Thus, $E_{n,k}^{(2)}$ simply becomes the second term on the lefthand side, for which Eq. (7.80) can be used as summarized below.

Second Order Correction for the Degenerate Eigenvalue

Employing Eq. (7.80) for the second term on the lefthand side of Eq. (7.82), we obtain

$$E_{n,k}^{(2)} = \sum_{m\neq n}\sum_{k=1}^{d} \frac{\langle\phi_{n,k}^{(0)}|\hat{H}_1|\psi_m^{(0)}\rangle\langle\psi_m^{(0)}|\hat{H}_1|\phi_{n,k}^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}. \quad (7.83)$$

Note that the sum involving degenerate states with the unknown coefficients $D_j^{(1)}$ in Eq. (7.80) do not contribute to the above term because $\langle\phi_{n,k}^{(0)}|\hat{H}_1|\phi_{n,j}^{(0)}\rangle = 0$ for $j \neq k$.

As the next step, let us take inner product of Eq. (7.81) with $\langle\phi_{n,j}^{(0)}|$ for $j \neq k$. Thus,

$$\langle\phi_{n,j}^{(0)}|\hat{H}_0|\phi_{n,k}^{(2)}\rangle + \langle\phi_{n,j}^{(0)}|\hat{H}_1|\phi_{n,k}^{(1)}\rangle = E_n^{(0)}\langle\phi_{n,j}^{(0)}|\phi_{n,k}^{(2)}\rangle + E_{n,k}^{(1)}\langle\phi_{n,j}^{(0)}|\phi_{n,k}^{(1)}\rangle, \quad (7.84)$$

where the fact that $\langle\phi_{n,j}^{(0)}|\phi_{n,k}^{(0)}\rangle = 0$ has been used. On the lefthand side of the above equation, the first term, $\langle\phi_{n,j}^{(0)}|\hat{H}_0|\phi_{n,k}^{(2)}\rangle = E_n^{(0)}\langle\phi_{n,j}^{(0)}|\phi_{n,k}^{(2)}\rangle$, cancels out with the same term on the righthand side. Therefore, the above equation reduces to

$$\langle\phi_{n,j}^{(0)}|\hat{H}_1|\phi_{n,k}^{(1)}\rangle = E_{n,k}^{(1)}\langle\phi_{n,j}^{(0)}|\phi_{n,k}^{(1)}\rangle. \quad (7.85)$$

This equation can be used to determine the $D_j^{(1)}$ in Eq. (7.80). Employing Eq. (7.80) in the above equation, we obtain

$$D_j^{(1)}E_{n,j}^{(1)} + \sum_{m\neq n}\sum_{k=1}^{d}\frac{\langle\phi_{n,j}^{(0)}|\hat{H}_1|\psi_m^{(0)}\rangle\langle\psi_m^{(0)}|\hat{H}_1|\phi_{n,k}^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}} = D_j^{(1)}E_{n,k}^{(1)}. \quad (7.86)$$

Assuming that $E_{n,j}^{(1)} \neq E_{n,k}^{(1)}$, the above equation can be solved for $D_j^{(1)}$ as follows:

$$D_j^{(1)} = \sum_{m\neq n}\sum_{k=1}^{d}\frac{\langle\phi_{n,j}^{(0)}|\hat{H}_1|\psi_m^{(0)}\rangle\langle\psi_m^{(0)}|\hat{H}_1|\phi_{n,k}^{(0)}\rangle}{(E_{n,k}^{(1)} - E_{n,j}^{(1)})(E_n^{(0)} - E_m^{(0)})}. \quad (7.87)$$

This completes the first order perturbation correction for degenerate states as summarized below.

First Order Correction for the Degenerate Eigenstate (Complete)

Using Eq. (7.87) in Eq. (7.80), we obtain the following expression for the complete first order expansion of $|\phi_{n,k}^{(1)}\rangle$:

$$|\phi_{n,k}^{(1)}\rangle = \sum_{j\neq k}^{d}\sum_{m\neq n}\frac{|\phi_{n,j}^{(0)}\rangle\langle\phi_{n,j}^{(0)}|\hat{H}_1|\psi_m^{(0)}\rangle\langle\psi_m^{(0)}|\hat{H}_1|\phi_{n,k}^{(0)}\rangle}{(E_{n,k}^{(1)} - E_{n,j}^{(1)})(E_n^{(0)} - E_m^{(0)})} + \sum_{m\neq n}\frac{|\psi_m^{(0)}\rangle\langle\psi_m^{(0)}|\hat{H}_1|\phi_{n,k}^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}. \quad (7.88)$$

Finally, let us take inner product of Eq. (7.86) with $\langle\psi_m^{(0)}|$ for $m \neq n$. Then, employing the fact that $\langle\psi_m^{(0)}|\hat{H}_0|\phi_{n,k}^{(2)}\rangle = E_m^{(0)}\langle\psi_m^{(0)}|\phi_{n,k}^{(2)}\rangle$ and $\langle\psi_m^{(0)}|\phi_{n,k}^{(0)}\rangle = 0$, we

obtain

$$E_m^{(0)}\langle\psi_m^{(0)}|\phi_{n,k}^{(2)}\rangle + \langle\psi_m^{(0)}|\hat{H}_1|\phi_{n,k}^{(1)}\rangle = E_n^{(0)}\langle\psi_m^{(0)}|\phi_{n,k}^{(2)}\rangle + E_{n,k}^{(1)}\langle\psi_m^{(0)}|\phi_{n,k}^{(1)}\rangle. \quad (7.89)$$

Solving this equation for $\langle\psi_m^{(0)}|\phi_{n,k}^{(2)}\rangle$, we obtain

$$\begin{aligned}\langle\psi_m^{(0)}|\phi_{n,k}^{(2)}\rangle &= \frac{\langle\psi_m^{(0)}|(\hat{H}_1 - E_{n,k}^{(1)})|\phi_{n,k}^{(1)}\rangle}{E_n^{(0)} - E_m^{(0)}} \\ &= \frac{1}{E_n^{(0)} - E_m^{(0)}}\left[\sum_{j\neq k}^{d}\sum_{m'\neq n}\frac{\langle\psi_m^{(0)}|\hat{H}_1|\phi_{n,j}^{(0)}\rangle\langle\phi_{n,j}^{(0)}|\hat{H}_1|\psi_{m'}^{(0)}\rangle\langle\psi_{m'}^{(0)}|\hat{H}_1|\phi_{n,k}^{(0)}\rangle}{(E_{n,k}^{(1)} - E_{n,j}^{(1)})(E_n^{(0)} - E_{m'}^{(0)})}\right. \\ &\qquad + \sum_{m'\neq n}\frac{\langle\psi_m^{(0)}|\hat{H}_1|\psi_{m'}^{(0)}\rangle\langle\psi_{m'}^{(0)}|\hat{H}_1|\phi_{n,k}^{(0)}\rangle}{E_n^{(0)} - E_{m'}^{(0)}} \\ &\qquad \left. - \frac{E_{n,k}^{(1)}\langle\psi_m^{(0)}|\hat{H}_1|\phi_{n,k}^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}\right]. \end{aligned} \quad (7.90)$$

The above expressions determines the expansion coefficients of $|\phi_{n,k}^{(2)}\rangle$ with respect to the $|\psi_m^{(0)}\rangle$ for $m \neq n$. However, the expansion coefficients of $|\phi_{n,k}^{(2)}\rangle$ with respect to the $|\phi_{n,j}^{(0)}\rangle$ with $j \neq k$ remain yet unknown, which can be determined only by solving the third order terms of the perturbation theory.

7.3 Summary and Questions

The variational principle results from the boundedness of the ground state energy for a stable quantum system, and thus offers an important guideline for approximating the ground state energy. Proving the variational principle is simple, and is based on the completeness of the eigenstates of a Hamiltonian. However, finding out an actual approximation is not always straightforward. Given that it is possible to identify a reasonable basis states that can be used to represent a trial state as a linear combination, it is possible to reduce the variational principle to a set of linear equations involving coefficients and eigenvalues, Eq. (7.18). Eigenvalues of this equation can be determined by solving Eq. (7.19). Employing these solutions in Eq. (7.18), one can then determine corresponding eigenstates. The resulting eigenstates, even when expanded in terms of nonorthogonal basis states, are orthogonal for different eigenvalues and can also be made to be orthogonal between states with the same eigenvalue.

The time independent perturbation theory provides general expressions for approximate eigenvalues and eigenstates of a Hamiltonian, which is given by a

sum of the zeroth order and small perturbation terms. The solutions are provided in terms of those for the zeroth order Hamiltonian. The reason for why this is always possible is because the eigenstates of the zeroth order Hamiltonian forms a complete basis. For the case where there is no degeneracy in the zeroth order Hamiltonian, perturbation corrections for the energies and states can be obtained by comparison of terms of the same order of the perturbation and projecting them to different eigenstates of the zeroth order Hamiltonian. The resulting corrections for the eigenvalues and eigenstates up to the second order of the perturbation are given by Eqs. (7.66) and (7.67).

However, for the case where there is degeneracy in the zeroth order Hamiltonian, the expressions obtained for the non-degenerate case become singular, and the theory should be developed in a slightly different manner. It turns out that identifying the best zeroth order eigenstates that suit the type of the Hamiltonian should precede determination of higher order terms. Diagonalizing the perturbation Hamiltonian in the space of degenerate states of the zeroth order Hamiltonian solves this issue. Thus, the first order corrections for the eigenvalues are given by solutions of Eq. (7.76) and the zeroth eigenstates are given by Eq. (7.78). Further consideration of higher order corrections including those of other non-degenerate components leads to the expression for the second order correction for the energy, Eq. (7.83), and the first correction for the state, Eq. (7.88).

Questions

- How general is the variational principle? Is there any possible exception where it is inapplicable?
- In applying the variational principle, it is common to approximate the trial state as a linear combination of predetermined basis states. What are benefits and limitations of this approximation?
- Is it possible to extend the variational principle for the calculation of excited state energies?
- For the case where the trial state is given by a linear combination of basis states, solving an eigenvalue equation produces many states and energies as solutions of the variational principle. Can all the higher energy states, except for the lowest energy state, be also used as solutions of the starting time independent Schrödinger equation?
- How can we examine the accuracy of a particular outcome of the variational theory?
- Expressions for the non-degenerate perturbation theory are inapplicable for the case where there is degeneracy in the zeroth order Hamiltonian. What is the reason for this?
- Are the states obtained from the perturbation theory normalized?
- How can we assess the accuracy of a particular application of the perturbation theory?

(continued)

- Let us assume that a hydrogen atom is subject to an external electric field. How can we apply the perturbation theory to calculate the effect of the electric field on the energy of the electron in this case?

Exercise Problems with Solutions

7.1 A certain Hamiltonian can be expressed as

$$\hat{H} = -|\varphi_1\rangle\langle\varphi_1| + |\varphi_2\rangle\langle\varphi_2|,$$

where $|\varphi_1\rangle$ and $|\varphi_2\rangle$ are normalized but are not orthogonal as follows:

$$\langle\varphi_1|\varphi_2\rangle = \langle\varphi_2|\varphi_1\rangle = \frac{1}{2}.$$

Use the variational theorem to determine the approximation for the ground state energy and express the corresponding approximate normalized ground state as a linear combination of $|\varphi_1\rangle$ and $|\varphi_2\rangle$.

Solution 7.1 For the given Hamiltonian,

$$\langle\varphi_1|\hat{H}|\varphi_1\rangle = -1 + \frac{1}{4} = -\frac{3}{4},$$

$$\langle\varphi_2|\hat{H}|\varphi_2\rangle = -\frac{1}{4} + 1 = \frac{3}{4},$$

$$\langle\varphi_1|\hat{H}|\varphi_2\rangle = -\frac{1}{2} + \frac{1}{2} = 0 = \langle\varphi_2|\hat{H}|\varphi_1\rangle.$$

The corresponding secular equation that results from the variational principle for this case is $\begin{vmatrix} -\frac{3}{4} - E & -\frac{1}{2}E \\ -\frac{1}{2}E & \frac{3}{4} - E \end{vmatrix} = \frac{3}{4}(E^2 - \frac{3}{4}) = 0$. This results in $E = \pm\frac{\sqrt{3}}{2}$. Therefore, the approximation for the ground state energy is $E_g = -\frac{\sqrt{3}}{2}$.

For E_g, we can find the approximate solution by solving the following matrix equation: $\begin{pmatrix} -\frac{3}{4} + \frac{\sqrt{3}}{2} & \frac{\sqrt{3}}{4} \\ \frac{\sqrt{3}}{4} & \frac{3}{4} + \frac{\sqrt{3}}{2} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0$.

Solving the above equation, we find that $C_2 = (\sqrt{3} - 2)C_1$. Thus,

$$|\psi_g\rangle = C_1 \left(|\varphi_1\rangle + (\sqrt{3} - 2)|\varphi_2\rangle\right).$$

Assuming the normalization condition,

$$\langle\psi_g|\psi_g\rangle = C_1^2\left(1 + 2(\sqrt{3}-2)\frac{1}{2} + 7 - 4\sqrt{3}\right) = 1,$$

we find that

$$C_1 = \frac{1}{\sqrt{6-3\sqrt{3}}}.$$

Therefore,

$$|\psi_g\rangle = \frac{1}{\sqrt{6-3\sqrt{3}}}|\varphi_1\rangle + \frac{\sqrt{3}-2}{\sqrt{6-3\sqrt{3}}}|\varphi_2\rangle.$$

7.2 Consider the Hamiltonian of a hydrogen-like system for the case where $l = 0$. In this case, the angular part becomes constant, and one can consider the radial part only. In other words, the Hamiltonian effectively becomes one dimensional as follows:

$$\hat{H} = -\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) - \frac{Ze^2}{4\pi\epsilon_0 r}.$$

Then, assuming that a trial wave function, $\phi(r) = e^{-\alpha r^2}$, where α is a free parameter, use the variational principle to calculate approximate ground state energy.

Solution 7.2 For the given trial wavefunction,

$$\begin{aligned}\langle\phi|\phi\rangle &= \int d\mathbf{r}|\phi(r)|^2 = 4\pi\int_0^\infty dr r^2 e^{-2\alpha r^2}\\ &= 4\pi\frac{1}{2}\frac{\sqrt{\pi}}{2(2\alpha)^{3/2}} = \frac{\pi^{3/2}}{2\sqrt{2}\alpha^{3/2}}.\end{aligned}$$

On the other hand,

$$\begin{aligned}\langle\phi|\hat{H}|\phi\rangle &= \int d\mathbf{r}\phi^*(r)\hat{H}\phi(r)\\ &= 4\pi\int_0^\infty dr r^2 e^{-\alpha r^2}\left(-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) - \frac{Ze^2}{4\pi\epsilon_0 r}\right)e^{-\alpha r^2}\\ &= 4\pi\int_0^\infty dr r^2 e^{-\alpha r^2}\left(-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(-2\alpha r^3 e^{-\alpha r^2}\right) - \frac{Ze^2}{4\pi\epsilon_0 r}e^{-\alpha r^2}\right)\end{aligned}$$

$$= 4\pi \int_0^\infty drr^2 \left(\frac{3\alpha\hbar^2}{\mu} - \frac{2\hbar^2\alpha^2}{\mu} r^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \right) e^{-2\alpha r^2}$$

$$= 4\pi \left(\frac{3\alpha\hbar^2}{\mu} \int_0^\infty drr^2 e^{-2\alpha r^2} - \frac{2\hbar^2\alpha^2}{\mu} \int_0^\infty drr^4 e^{-2\alpha r^2} - \frac{Ze^2}{4\pi\epsilon_0} \int_0^\infty drre^{-2\alpha r^2} \right).$$

Employing the following identities for the integrals:

$$\int_0^\infty drr^2 e^{-2\alpha r^2} = \frac{1}{2} \int_{-\infty}^\infty r^2 e^{-2\alpha r^2} = \frac{\sqrt{\pi}}{4(2\alpha)^{3/2}},$$

$$\int_0^\infty drr^4 e^{-2\alpha r^2} = \frac{1}{2} \int_{-\infty}^\infty r^4 e^{-2\alpha r^2} = \frac{3\sqrt{\pi}}{8(2\alpha)^{5/2}},$$

$$\int_0^\infty drre^{-2\alpha r^2} = \frac{1}{4\alpha},$$

$\langle\phi|\hat{H}|\phi\rangle$ can be simplified as

$$\langle\phi|\hat{H}|\phi\rangle = 4\pi \left(\frac{3\alpha\hbar^2}{\mu} \frac{\sqrt{\pi}}{4(2\alpha)^{3/2}} - \frac{2\hbar^2\alpha^2}{\mu} \frac{3\sqrt{\pi}}{8(2\alpha)^{5/2}} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{4\alpha} \right)$$

$$= \frac{4\pi^{3/2}\hbar^2}{2\mu\sqrt{\alpha}} \left(\frac{3}{4\sqrt{2}} - \frac{3}{8\sqrt{2}} \right) - \frac{Ze^2}{4\epsilon_0\alpha}$$

$$= \frac{3\pi^{3/2}\hbar^2}{4\sqrt{2}\mu\sqrt{\alpha}} - \frac{Ze^2}{4\epsilon_0\alpha}.$$

Therefore,

$$E_\phi = E(\alpha) = \left(\frac{3\pi^{3/2}\hbar^2}{4\sqrt{2}\mu\sqrt{\alpha}} - \frac{Ze^2}{4\epsilon_0\alpha} \right) \frac{2\sqrt{2}\alpha^{3/2}}{\pi^{3/2}}$$

$$= \frac{3\hbar^2\alpha}{2\mu} - \frac{Ze^2\sqrt{\alpha}}{\sqrt{2}\epsilon_0\pi^{3/2}}.$$

Now, taking the derivative of $E(\alpha)$ with respect to α and using the following necessary condition for it to be a minimum:

$$\frac{dE(\alpha)}{d\alpha} = \frac{3\hbar^2}{2\mu} - \frac{Ze^2}{2\sqrt{2}\epsilon_0\pi^{3/2}} \frac{1}{\sqrt{\alpha}} = 0,$$

we find that

$$\alpha = \left(\frac{Ze^2}{2\sqrt{2}\epsilon_0\pi^{3/2}}\frac{2\mu}{3\hbar^2}\right)^2 = \frac{Z^2e^4\mu^2}{18\pi^3\hbar^4\epsilon_0^2}.$$

For this value of α, the energy given by E_ϕ becomes

$$\begin{aligned} E &= \frac{3\hbar^2}{2\mu}\frac{Z^2e^4\mu^2}{18\pi^3\hbar^4\epsilon_0^2} - \frac{Ze^2}{\sqrt{2}\epsilon_0\pi^{3/2}}\frac{Ze^2\mu}{\sqrt{2}\epsilon_0\pi^{3/2}3\hbar^2} \\ &= \frac{\mu Z^2e^4}{12\pi^3\hbar^2\epsilon_0^2} - \frac{\mu Z^2e^4}{6\pi^3\hbar^2\epsilon_0^2} = -\frac{\mu Z^2e^4}{12\pi^3\hbar^2\epsilon_0^2} = -\frac{32}{12\pi}\frac{\mu Z^2e^4}{32\pi^2\epsilon_0^2\hbar^2} \\ &= -0.849E_g, \end{aligned}$$

where E_g is the true ground state.

7.3 Prove that the states $|\phi_+\rangle$ and $|\phi_-\rangle$ given by Eqs. (7.34) and (7.35) are variational eigenstates corresponding to the variational energies, Eqs. (7.32) and (7.33), respectively.

Solution 7.3 For $E_+ = (H_d + H_c)/(1+S)$,

$$\begin{pmatrix} H_d - E_+ & H_c - E_+S \\ H_c - E_+S & H_d - E_+ \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \frac{H_dS - H_c}{1+S}\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0.$$

This means that $C_1 = C_2$. Thus,

$$|\phi_+\rangle = C_1(|f_1\rangle + |f_2\rangle).$$

The norm of this is as follows:

$$\langle\phi_+|\phi_+\rangle = |C_1|^2\,(1+1+2S) = 2|C_1|^2(1+S).$$

Thus, $C_1 = 1/\sqrt{2(1+S)}$.

For $E_- = (H_d - H_c)/(1-S)$,

$$\begin{pmatrix} H_d - E_- & H_c - E_-S \\ H_c - E_-S & H_d - E_- \end{pmatrix}\begin{pmatrix} C_1' \\ C_2' \end{pmatrix} = \frac{H_c - H_dS}{1-S}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}\begin{pmatrix} C_1' \\ C_2' \end{pmatrix} = 0.$$

This means that $C_1' = -C_2'$. Thus,

$$|\phi_+\rangle = C_1'(|f_1\rangle - |f_2\rangle).$$

The norm of this is as follows:

$$\langle \phi_- | \phi_- \rangle = |C_1'|^2 \,(1 + 1 - 2S) = 2|C_1'|^2 (1 - S).$$

Thus, $C_1' = 1/\sqrt{2(1-S)}$.

7.4 Consider a harmonic oscillator with linear perturbation as follows:

$$\hat{H}_0 = \frac{\hat{p}^2}{2\mu} + \frac{1}{2}\mu\omega^2\hat{x}^2, \tag{7.91}$$

$$\hat{H}_1 = C\hat{x}. \tag{7.92}$$

Use the non-degenerate perturbation theory to determine perturbation corrections of the eigenvalue up to the second order and the eigenstate up to the first order.

Solution 7.4 Then, $|\psi_v^{(0)}\rangle = |v\rangle$, where

$$\hat{H}_0|v\rangle = \hbar\omega(v + \frac{1}{2})|v\rangle. \tag{7.93}$$

It is straightforward to show that

$$\langle v|\hat{H}_1|v'\rangle = C\sqrt{\frac{\hbar}{2\mu\omega}}\left(\sqrt{v+1}\,\delta_{v',v+1} + \sqrt{v}\,\delta_{v',v-1}\right). \tag{7.94}$$

Therefore,

$$E_v^{(1)} = \langle v|\hat{H}_1|v\rangle = 0, \tag{7.95}$$

$$\begin{aligned} E_v^{(2)} &= \sum_{v' \neq v} \frac{\langle v'|\hat{H}_1|v\rangle\langle v|\hat{H}_1|v'\rangle}{\hbar\omega(v - v')} \\ &= \left(\frac{(\sqrt{v})^2}{\hbar\omega} - \frac{(\sqrt{v+1})^2}{\hbar\omega}\right) C^2\frac{\hbar}{2\mu\omega} = -\frac{C^2\hbar}{2\hbar\omega^2\mu} = -\frac{C^2}{2\mu\omega^2}. \end{aligned} \tag{7.96}$$

Combining the above expressions, we find that

$$E_v = E_v^{(0)} + E_v^{(1)} + E_v^{(2)} = \hbar(v + \frac{1}{2}) - \frac{C^2}{2\mu\omega^2}. \tag{7.97}$$

In fact, one can show that this is an exact value employing the following identity:

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \frac{1}{2}\mu\omega^2\hat{x}^2 + c\hat{x} \tag{7.98}$$

$$= \frac{\hat{p}^2}{2\mu} + \frac{1}{2}\mu\omega^2\left(\hat{x}^2 + \frac{2C}{\mu\omega^2}\hat{x} + \frac{C^2}{\mu^2\omega^4}\right) - \frac{1}{2}\frac{C^2}{\mu\omega^2}$$

$$= \frac{\hat{p}^2}{2\mu} + \frac{1}{2}\mu\omega^2\left(\hat{x} + \frac{C}{\mu\omega^2}\right)^2 - \frac{1}{2}\frac{C^2}{\mu\omega^2}$$

$$= \frac{\hat{p}^2}{2\mu} + \frac{1}{2}\mu\hat{X}^2 - \frac{1}{2}\frac{C^2}{\mu\omega^2}, \tag{7.99}$$

where $\hat{X} = \hat{x} + \frac{C}{\mu\omega^2}$. On the other hand, the eigenstate, up to the first order is given by

$$|\psi_v\rangle = |v\rangle + \frac{C}{\hbar\omega}\sqrt{\frac{\hbar}{2\mu\omega}}\left\{\sqrt{v}|v-1\rangle - \sqrt{v+1}|v+1\rangle\right\}. \tag{7.100}$$

7.5 The zeroth order Hamiltonian of a certain system is given by $\hat{H}_0 = |\phi_1\rangle\langle\phi_1| + 2|\phi_2\rangle\langle\phi_2|$, where $|\phi_1\rangle$ and $|\phi_2\rangle$ are orthonormal sates. A perturbation Hamiltonian $\hat{H}_1$ is added to $\hat{H}_0$, and the expression for $\hat{H}_1$ is as follows:

$$\hat{H}_1 = \frac{1}{2}\left(|\phi_1\rangle\langle\phi_1| + |\phi_2\rangle\langle\phi_2|\right) + \frac{1}{4}\left(|\phi_1\rangle\langle\phi_2| + |\phi_2\rangle\langle\phi_1|\right).$$

Calculate the first order and second order perturbation energy corrections for the two eigenvalues of $\hat{H}_0$.

Solution 7.5 Note that $|\phi_1\rangle$ and $|\phi_2\rangle$ are eigenstates of $\hat{H}_0$ with eigenvalues $E_1^{(0)} = 1$ and $E_2^{(0)} = 2$ respectively. Therefore,

$$E_1^{(1)} = \langle\phi_1|\hat{H}_1|\phi_1\rangle = \frac{1}{2} \quad \& \quad E_2^{(1)} = \langle\phi_2|\hat{H}_1|\phi_2\rangle = \frac{1}{2}$$

$$E_1^{(2)} = \frac{|\langle\phi_1|\hat{H}_1|\phi_2\rangle|^2}{E_1^{(0)} - E_2^{(0)}} = -\frac{1}{16} \quad \& \quad E_2^{(2)} = \frac{|\langle\phi_2|\hat{H}_1|\phi_1\rangle|^2}{E_2^{(0)} - E_1^{(0)}} = \frac{1}{16}$$

7.6 Consider a Hamiltonian $\hat{H}$ defined as follows:

$$\hat{H} = a|1\rangle\langle 1| + 2a|2\rangle\langle 2| + 3a|3\rangle\langle 3|,$$

where $|1\rangle$, $|2\rangle$, and $|3\rangle$ are orthonormal states and a is a positive real number. Answer the following questions.

(a) For any state $|\phi\rangle = C_1|1\rangle + C_2|2\rangle + C_3|3\rangle$, find out the expression for E_ϕ.
(b) Determine the minimum and maximum values of E_ϕ and corresponding state $|\phi\rangle$ for each case.
(c) Assume $|\phi\rangle$ as a variational trial state, write down the matrix equation Eq. (7.18) for the Hamiltonian $\hat{H}$, determine three variational energies and states.
(d) A small perturbation term $\hat{H}_1$ is added to the Hamiltonian so that the total Hamiltonian changes to $\hat{H}' = \hat{H} + \hat{H}_1$, where

$$\hat{H}_1 = \frac{a}{5}(|1\rangle\langle 2| + |2\rangle\langle 1|).$$

Find out the first order approximation for the ground eigenstate and second order approximation for the ground state energy.

Solution 7.6 Let us first calculate $\langle\phi|\hat{H}|\phi\rangle$ and $\langle\phi|\phi\rangle$ as follows:

$$\begin{aligned}
\langle\phi|\hat{H}|\phi\rangle &= \left(C_1^*\langle 1| + C_2^*\langle 2| + C_3^*\langle 3|\right)(a|1\rangle\langle 1| + 2a|2\rangle\langle 2| + 3a|3\rangle\langle 3|) \\
&\qquad \times (C_1|1\rangle + C_2|2\rangle + C_3|3\rangle) \\
&= \left(C_1^*\langle 1| + C_2^*\langle 2| + C_3^*\langle 3|\right)(aC_1|1\rangle + 2aC_2|2\rangle + 3aC_3|3\rangle) \\
&= a|C_1|^2 + 2a|C_2|^2 + 3a|C_3|^2, \\
\langle\phi|\phi\rangle &= |C_1|^2 + |C_2|^2 + |C_3|^2.
\end{aligned}$$

(a) The expectation value E_ϕ can be expressed as follows:

$$E_\phi = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle} = a\frac{|C_1|^2 + 2|C_2|^2 + 3|C_3|^2}{|C_1|^2 + |C_2|^2 + |C_3|^2}.$$

(b) Let us introduce the following normalized coefficients:

$$\tilde{C}_1 = \frac{C_1}{\sqrt{|C_1|^2 + |C_2|^2 + |C_3|^2}},$$

$$\tilde{C}_2 = \frac{C_2}{\sqrt{|C_1|^2 + |C_2|^2 + |C_3|^2}},$$

$$\tilde{C}_3 = \frac{C_3}{\sqrt{|C_1|^2 + |C_2|^2 + |C_3|^2}}.$$

Then,

$$\begin{aligned} E_\phi &= a\left(|\tilde{C}_1|^2 + 2|\tilde{C}_2|^2 + 3|\tilde{C}_3|^2\right) \\ &= a\left(1 + |\tilde{C}_2|^2 + 2|\tilde{C}_3|^2\right) \\ &= a\left(3 - 2|\tilde{C}_1|^2 - |\tilde{C}_1|^2\right), \end{aligned}$$

where the fact that $|\tilde{C}_1|^2+|\tilde{C}_2|^2+|\tilde{C}_3|^2 = 1$ has been used. The second equality of the above expressions shows that the minimum value E_ϕ is a, which occurs when $C_2 = C_3 = 0$ and the third equality shows that the maximum value of E_ϕ is $3a$, which occurs when $C_1 = C_2 = 0$.

(c) For the given Hamiltonian, $H_{11} = a$, $H_{22} = 2a$, and $H_{33} = 3a$ and all other terms are zero. On the other hand, $S_{ij} = \delta_{ij}$. Therefore,

$$\begin{pmatrix} a - E & 0 & 0 \\ 0 & 2a - E & 0 \\ 0 & 0 & 3a - E \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}.$$

The above matrix is already diagonal. Thus, the three values of E are a, $2a$, and $3a$. The states corresponding to these values are respectively, $|1\rangle$, $|2\rangle$, and $|3\rangle$.

(d) The ground state is $|1\rangle$ and its energy is $E_1^{(0)} = a$. The first order perturbation energy is zero as can be seen below.

$$E_1^{(1)} = \langle 1|\hat{H}_1|1\rangle = \frac{a}{5}\left(\langle 1|1\rangle\langle 2|1\rangle + \langle 1|2\rangle\langle 1|1\rangle\right) = 0.$$

On the other hand, the coefficients for first order correction for the ground state are as follows:

$$\begin{aligned} C_2^{(1)} &= \frac{\langle 2|\hat{H}_1|1\rangle}{E_1^{(0)} - E_2^{(0)}} = \frac{a}{5}\frac{\langle 2|2\rangle\langle 1|1\rangle}{-a} = -\frac{1}{5}, \\ C_3^{(1)} &= 0. \end{aligned}$$

This implies that

$$|\psi_1^{(1)}\rangle = -\frac{1}{5}|2\rangle.$$

Therefore, up to the first order,

$$|\psi_1\rangle = |1\rangle - \frac{1}{5}|2\rangle.$$

The second order perturbation of the ground state energy is as follows:

$$E_1^{(2)} = \frac{\langle 2|\hat{H}_1|1\rangle\langle 1|\hat{H}_1|2\rangle}{E_1^{(0)} - E_2^{(0)}} = \frac{(a/5)^2}{a-2a} = -\frac{a}{25}.$$

Therefore, up to the second order of perturbation, the ground state energy becomes corrected to

$$E_1 = a - \frac{a}{25} = \frac{24}{25}a.$$

7.7 For a quantum particle of unit mass confined in a box of unit length, the eigenfunctions and eigenvalues are given by

$$\langle x|\psi_n\rangle = \psi_n(x) = \sqrt{2}\sin(n\pi x) \text{ for } 0 < x < 1,$$
$$E_n = \frac{\pi^2\hbar^2 n^2}{2},$$

where $n = 1, 2, 3, \cdots$. Now assume that the following potential energy is added inside the box:

$$V(x) = \begin{cases} \hbar^2 x/5\ , & 0 < x < 0.5 \\ \hbar^2(1-x)/5\ , & 0.5 < x < 1 \end{cases}$$

Therefore, the total Hamiltonian becomes

$$\hat{H} = \frac{\hat{p}^2}{2} + V(\hat{x}).$$

(a) Calculate the following matrix elements:

$$H_{11} = \langle\psi_1|\hat{H}|\psi_1\rangle,$$
$$H_{22} = \langle\psi_2|\hat{H}|\psi_2\rangle,$$
$$H_{12} = \langle\psi_1|\hat{H}|\psi_2\rangle = \langle\psi_2|\hat{H}|\psi_1\rangle = H_{21}.$$

(b) Consider a trial state given by the following linear combination

$$|\phi\rangle = C_1|\psi_1\rangle + C_2|\psi_2\rangle,$$

where C_1 and C_2 are real coefficients. Use the variational principle to determine the approximation for the ground state energy.

(c) Use $V(\hat{x})$ as a perturbation Hamiltonian, and calculate the first order perturbation approximation for the ground state energy.

Solution 7.7

(a) The matrix elements of the Hamiltonian can be calculated as follows:

$$
\begin{aligned}
H_{11} &= \langle\psi_1|\hat{H}|\psi_1\rangle \\
&= 2\int_0^1 dx \sin(\pi x)\left(-\frac{\hbar^2}{2}\frac{\partial^2}{\partial x^2}+V(x)\right)\sin(\pi x) \\
&= \hbar^2\left(\pi^2\int_0^1 dx \sin^2(\pi x) + 2\int_0^{1/2} dx \sin^2(\pi x)\frac{x}{5}\right. \\
&\qquad\qquad \left. +2\int_{1/2}^1 \sin^2(\pi x)\frac{1-x}{5}\right).
\end{aligned}
$$

In the above expression,

$$
\begin{aligned}
\int_0^{1/2} dx \sin^2(\pi x)x &= \frac{1}{2}\int_0^{1/2} dx\ (1-\cos(2\pi x))\ x \\
&= \frac{1}{2}\int_0^{1/2} dx\ (x - x\cos(2\pi x)) = \frac{1}{16}+\frac{1}{4\pi^2}.
\end{aligned}
$$

Due to symmetry, $\int_{1/2}^1 \sin^2(\pi x)\frac{1-x}{5}$ has the same value. Therefore,

$$
H_{11} = \hbar^2\left(\frac{\pi^2}{2}+\frac{4}{5}\left(\frac{1}{16}+\frac{1}{4\pi^2}\right)\right) = \hbar^2\left(\frac{\pi^2}{2}+\frac{1}{20}+\frac{1}{5\pi^2}\right).
$$

Similarly,

$$
\begin{aligned}
H_{22} &= \langle\psi_2|\hat{H}|\psi_2\rangle = 2\int_0^1 dx \sin(2\pi x)\left(-\frac{\hbar^2}{2}\frac{d^2}{dx^2}+V(x)\right)\sin(2\pi x) \\
&= \hbar^2\left(\frac{4\pi^2}{2}+2\int_0^1 dx \sin(2\pi x)V(x)\sin(2\pi x)\right) \\
&= \hbar^2\left(2\pi^2+\frac{4}{5}\int_0^{1/2} dx\frac{1}{2}\,(1-\cos(4\pi x))x)\right) \\
&= \hbar^2\left(2\pi^2+\frac{1}{20}\right).
\end{aligned}
$$

On the other hand,

$$\begin{aligned}
H_{12} = \langle \psi_1 | \hat{H} | \psi_2 \rangle &= 2 \int_0^1 dx \sin(\pi x) V(x) \sin(2\pi x) \\
&= \int_0^1 dx \, (\cos(\pi x) - \cos(3\pi x)) \, V(x) \\
&= \frac{\hbar^2}{5} \int_0^{1/2} dx \, (\cos(\pi x) - \cos(3\pi x)) \, x \\
&\quad + \frac{\hbar^2}{5} \int_{1/2}^{1} dx \, (\cos(\pi x) - \cos(3\pi x)) \, (1 - x) \\
&= \frac{\hbar^2}{5} \int_0^{1/2} dx \, (\cos(\pi x) - \cos(3\pi x)) \, x \\
&\quad + \frac{\hbar^2}{5} \int_0^{1/2} dx \, (\cos(\pi (1 - x)) - \cos(3\pi (1 - x))) \, x \\
&= \frac{\hbar^2}{5} \int_0^{1/2} dx \, (\cos(\pi x) - \cos(3\pi x)) \, x \\
&\quad - \frac{\hbar^2}{5} \int_0^{1/2} dx \, (\cos(\pi x) - \cos(3\pi x)) \, x = 0.
\end{aligned}$$

(b) For the given trial state,

$$\begin{pmatrix} H_{11} - E & 0 \\ 0 & H_{22} - E \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}.$$

Since the matrix is already diagonal, the solutions are simply $E = H_{11}$ and E_{22}, for which the corresponding states are $|\phi\rangle = |\psi_1\rangle$ and $|\psi_2\rangle$, respectively.

(c) As shown in the answer for part (a),

$$\langle \psi_1 | V(\hat{x}) | \psi_1 \rangle = \frac{4\hbar^2}{5} \left(\frac{1}{16} + \frac{1}{4\pi^2} \right).$$

Therefore,

$$E_1^{(0)} + E_1^{(1)} = \hbar^2 \left(\frac{\pi^2}{2} + \frac{1}{20} + \frac{1}{5\pi^2} \right).$$

7.8 For a particle of unit mass confined in a box of unit length, assume that the following potential energy is added.

$$V(x) = \frac{\hbar^2}{2}\cos(\pi x).$$

Provide answers for (a), (b), and (c) in Problem 7.3 for this potential energy.

Solution 7.8

(a) The matrix elements of $\hat{V}$ can be calculated as follows:

$$\langle\psi_1|\hat{V}|\psi_1\rangle = 2\hbar^2\int_0^1 dx\,\sin^2(\pi x)\frac{1}{2}\cos(\pi x) = 0,$$

$$\langle\psi_2|\hat{V}|\psi_2\rangle = 2\hbar^2\int_0^1 dx\,\sin^2(2\pi x)\frac{1}{2}\cos(\pi x) = 0.$$

The fact that the above integrals are zero can be confirmed easily by noting that $\cos(\pi x)$ is antisymmetric with respect to $x = 1/2$ whereas $\sin^2(\pi x)$ and $\sin^2(2\pi x)$ are symmetric. On the other hand,

$$\begin{aligned}\langle\psi_1|\hat{V}|\psi_2\rangle &= \hbar^2\int_0^1 dx\,\sin(\pi x)\sin(2\pi x)\cos(\pi x)\\ &= \frac{\hbar^2}{2}\int_0^1 dx\left(\cos^2(\pi x) - \cos(\pi x)\cos(3\pi x)\right)\\ &= \frac{\hbar^2}{4}\int_0^1 dx\,(1+\cos(2\pi x) - \cos(2\pi x) - \cos(4\pi x)) = \frac{\hbar^2}{4}.\end{aligned}$$

Combining the above results with the eigenvalues of the zeroth order Hamiltonian, $H_{11} = \hbar^2\pi^2/2$, $H_{22} = 2\hbar^2\pi^2$, and $H_{12} = \hbar^2/4$.

(b) The coefficients C_1 and C_2 of the trial state satisfy the following matrix equation:

$$\begin{pmatrix} H_{11}-E & H_{12} \\ H_{12} & H_{22}-E \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}.$$

This is satisfied for nonzero coefficients only if the determinant is zero, which leads to the following equation for E:

$$(H_{11}-E)(H_{22}-E) - H_{12}^2 = 0.$$

The solutions for the above quadratic equation are as follows:

$$E = \frac{1}{2}(H_{11} + H_{22}) \pm \sqrt{\left(\frac{H_{11} - H_{22}}{2}\right)^2 + H_{12}^2}$$
$$= \hbar^2\pi^2 \left(\frac{5}{4} \pm \frac{3}{4}\sqrt{1 + \frac{1}{9\pi^4}}\right).$$

Thus, the variational approximation for the ground state energy is as follows:

$$E_g = \hbar^2\pi^2 \left(\frac{5}{4} - \frac{3}{4}\sqrt{1 + \frac{1}{9\pi^4}}\right)$$
$$\approx \hbar^2\pi^2 \left(1 - \frac{1}{24\pi^4}\right),$$

where the last line is an approximation but is a useful one with fairly good accuracy. The coefficients corresponding to the above ground state energy can be found by using the above energy in the matrix equation. The resulting relationship between C_1 and C_2 is as follows:

$$C_2 = -\frac{1}{H_{12}}\left\{\frac{1}{2}(H_{11} - H_{22}) + \sqrt{\left(\frac{H_{11} - H_{22}}{2}\right)^2 + H_{12}^2}\right\} C_1$$
$$= 3\pi^2 \left(1 - \sqrt{1 + \frac{1}{9\pi^4}}\right) C_1 \approx -\frac{1}{6\pi^2} C_1.$$

Then, C_1 can be determined by the normalization condition.

(c) Since $\langle\psi_1|\hat{V}|\psi_1\rangle = 0$, there is no first order correction for the ground state energy.

7.9 The zeroth order Hamiltonian of a certain system is given by

$$\hat{H}_0 = |\phi_1\rangle\langle\phi_1| + |\phi_2\rangle\langle\phi_2| + |\phi_3\rangle\langle\phi_3|,$$

where $|\phi_1\rangle$, $|\phi_2\rangle$, and $|\phi_3\rangle$ are orthonormal sates. A perturbation Hamiltonian $\hat{H}_1$ is added to $\hat{H}_0$, and the expression for $\hat{H}_1$ is as follows:

$$\hat{H}_1 = \frac{1}{\sqrt{2}}(|\phi_1\rangle\langle\phi_2| + |\phi_2\rangle\langle\phi_1| + |\phi_2\rangle\langle\phi_3| + |\phi_3\rangle\langle\phi_2|).$$

Use the degenerate perturbation theory to determine the lowest value of the first order correction of the energy and the corresponding zeroth order ground state.

Solution 7.9 The equation for the determinant $|\hat{H}_1 - E| = 0$ is as follows:

$$\begin{vmatrix} -E & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & -E & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & -E \end{vmatrix} = -E^3 + \frac{1}{2}E + \frac{1}{2}E = -E(E-1)(E+1) = 0.$$

Therefore, the lowest value of the first order perturbation correction is -1.

To find the zeroth order state corresponding this value, we need to solve the following matrix equation.

$$\begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & 0 \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix} = - \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix}.$$

The resulting coefficients satisfying the normalization condition are $C_1 = C_3 = 1/2$ and $C_2 = -\frac{1}{\sqrt{2}}$. Thus, the zeroth order state corresponding to $E^{(1)} = -1$ is $(|\phi_1\rangle - \sqrt{2}|\phi_2\rangle + |\phi_3\rangle)/2$.

7.10 Consider a zeroth order Hamiltonian $\hat{H}_0$ defined as follows:

$$\hat{H} = b|1\rangle\langle 1| + b|2\rangle\langle 2| + 2b|3\rangle\langle 3|,$$

where $|1\rangle$, $|2\rangle$, and $|3\rangle$ are orthonormal states and b is a positive real number. A small perturbation term $\hat{H}_1$ is added to the Hamiltonian so that the total Hamiltonian changes to $\hat{H} = \hat{H}_0 + \hat{H}_1$, where

$$\hat{H}_1 = \frac{b}{3}(|1\rangle\langle 2| + |2\rangle\langle 1|).$$

Use the degenerate perturbation theory to find out the first order correction for the ground state energy and the zeroth order correction for the ground eigenstate.

Solution 7.10 In the space of $|1\rangle$ and $|2\rangle$, $\langle 1|\hat{H}_1|1\rangle = \langle 2|\hat{H}_1|2\rangle = 0$ and $\langle 1|\hat{H}_1|2\rangle = b/3$. Therefore, according to the degenerate perturbation theory,

$$\begin{vmatrix} -\lambda & \frac{b}{3} \\ \frac{b}{3} & -\lambda \end{vmatrix} = \lambda^2 - \left(\frac{b}{3}\right)^2 = 0.$$

The solution of this is that $\lambda = \pm b/3$. Therefore, the energy of the state 1 that is corrected up to the first order is as follows:

$$E_1^{(0)} + E_1^{(1)} = b - \frac{b}{3} = \frac{2}{3}b.$$

The zeroth order eigenstate corresponding to this energy can be determined by solving the following matrix equation:

$$\begin{pmatrix} \frac{b}{3} & \frac{b}{3} \\ \frac{b}{3} & \frac{b}{3} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix},$$

which results in $C_1 + C_2 = 0$. Thus, after normalization, the zeroth order state can be expressed as follows:

$$|\phi_1^{(0)}\rangle = \frac{1}{\sqrt{2}} \left(|1\rangle - |2\rangle \right).$$

Problems

7.11 For a particle with unit mass subject to the following potential:

$$V(x) = \frac{9}{16} \hbar^2 x^4.$$

Use the following trial wavefunction $\phi(x) = e^{-\alpha x^2/2}$ and the variational principle to determine the best value α approximating the ground state wavefunction and the best approximation for the ground state energy.

7.12 A zeroth order Hamiltonian $\hat{H}_0$ is given by

$$\hat{H}_0 = |\phi_1\rangle\langle\phi_1| + 2|\phi_2\rangle\langle\phi_2| + 3|\phi_3\rangle\langle\phi_3|,$$

where $|\phi_1\rangle$, $|\phi_2\rangle$, and $|\phi_3\rangle$ are normalized and orthogonal to each other. Given that the following perturbation Hamiltonian is added,

$$\begin{aligned} \hat{H}_1 = & \frac{1}{4}|\phi_1\rangle\langle\phi_1| + \frac{1}{2}|\phi_2\rangle\langle\phi_2| \\ & + \frac{1}{2}|\phi_2\rangle\langle\phi_3| + \frac{1}{2}|\phi_3\rangle\langle\phi_2| - \frac{1}{2}|\phi_1\rangle\langle\phi_3| - \frac{1}{2}|\phi_3\rangle\langle\phi_1|, \end{aligned}$$

answer the following questions.

(a) Determine the first order perturbation corrections for all the eigenvalues and eigenstates of $\hat{H}_0$.
(b) Determine the second order perturbation corrections for all the eigenvalues of $\hat{H}_0$.

7.13 A zeroth order Hamiltonian $\hat{H}_0$ is given by

$$\hat{H}_0 = |\phi_1\rangle\langle\phi_1| + |\phi_2\rangle\langle\phi_2| + |\phi_3\rangle\langle\phi_3|,$$

which has degeneracy of 3. Note that $|\phi_1\rangle$, $|\phi_2\rangle$, and $|\phi_3\rangle$ are normalized and orthogonal to each other. Given that the following perturbation Hamiltonian is added,

$$\begin{aligned}\hat{H}_1 &= \lambda \left(|\phi_1\rangle\langle\phi_1| + 2|\phi_2\rangle\langle\phi_2| + 3|\phi_3\rangle\langle\phi_3|\right) \\ &+ \frac{\lambda}{2}\left(|\phi_1\rangle\langle\phi_2| + |\phi_2\rangle\langle\phi_1| - |\phi_2\rangle\langle\phi_3| - |\phi_3\rangle\langle\phi_2|\right).\end{aligned}$$

Use the degenerate perturbation theory to calculate the first order corrections for the eigenvalues of $\hat{H}_0$ and the corresponding zeroth order corrections for the eigenstates of $\hat{H}_0$.

Chapter 8
Many Electron Systems and Atomic Spectroscopy



The mathematical framework of quantum theory has passed countless successful tests and is now universally accepted as a consistent and accurate description of all atomic phenomena.

– Erwin Schrödinger

Abstract This chapter explains approximate quantum mechanical description of many electron (more than one) atoms and their electronic spectroscopy. A quick overview of independent electron model revisits well-established concepts of atomic orbitals and configurations, and clarifies approximations involved in such description. Symmetry properties of spin-orbit states and simple methods for determining atomic term symbols are described. Rules for determining relative energies of atomic terms and selection rules for atomic spectroscopy are clarified. The chapter then provides a more detailed mathematical account of independent electron approximations using helium atom as an example and then provides a general description of the self-consistent approximation for many electron atoms.

8.1 Hamiltonian

The Hamiltonian operator for atoms with many electrons is as follows:

$$\hat{H} = \frac{\hat{\mathbf{P}}_c^2}{2m_c} + \sum_{j=1}^{N_e} \left\{ \frac{\hat{\mathbf{p}}_j^2}{2m_e} + V_{en}(|\hat{\mathbf{r}}_j - \hat{\mathbf{R}}_c|) \right\} + \frac{1}{2} \sum_{j=1}^{N_e} \sum_{k \neq j} V_{ee}(|\hat{\mathbf{r}}_j - \hat{\mathbf{r}}_k|), \tag{8.1}$$

where $\hat{\mathbf{P}}_c$ and $\hat{\mathbf{R}}_c$ represent momentum and position operators of the nucleus, and $\hat{\mathbf{p}}_j$ and $\hat{\mathbf{r}}_j$ the momentum and position operators of the jth electron. m_c is the mass of the nucleus and m_e is the mass of the electron. N_e is the number of electrons, and the last term involves double summation over j and k running from 1 to N_e except that $j \neq k$. V_{en} and V_{ee} represent electron-nucleus and electron-electron Coulomb

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potential energy operators that are defined as

$$V_{en}(|\hat{\mathbf{r}}|) = -\frac{Ze^2}{4\pi\epsilon_0|\hat{\mathbf{r}}|}, \quad (8.2)$$

$$V_{ee}(|\hat{\mathbf{r}}|) = \frac{e^2}{4\pi\epsilon_0|\hat{\mathbf{r}}|}. \quad (8.3)$$

Although Eq. (8.1) is a simple extension of the Hamiltonian for hydrogen-like systems, the fact that it involves interactions of three or more particles causes the corresponding quantum mechanical problem much more challenging. In particular, the last electron-electron repulsion term makes it impossible to solve the corresponding Schrödinger equation exactly.

Assuming that the nucleus is fixed at the origin (or considering in such coordinate system), one can reduce Eq. (8.1) to the following many electron Hamiltonian:

$$\hat{H}_{el} = \sum_{j=1}^{N_e} \left\{ \frac{\hat{\mathbf{p}}_j^2}{2m_e} + V_{en}(\hat{r}_j) \right\} + \frac{1}{2} \sum_{j=1}^{N_e} \sum_{k \neq j} V_{ee}(|\hat{\mathbf{r}}_j - \hat{\mathbf{r}}_k|), \quad (8.4)$$

where $\hat{r}_j = |\hat{\mathbf{r}}_j|$. Even with this simplification, there is no exact analytic solution of the Schrödinger equation for this Hamiltonian for $N_e \geq 2$. Therefore, one has to rely on approximation methods. Due to the fact that electrons are fermions satisfying the Pauli exclusion principle, care should be taken in employing approximation methods. We will first start with the simplest approximation of assuming independent electrons, which can be justified with a proper application of the variational principle as will be detailed later in this chapter.

8.2 Independent Electron Model

8.2.1 Major Assumptions

At the simplest level, the effects of electron-electron interactions can be accounted for by introducing an effective single-electron potential, which modifies the original electron-nucleus Coulomb interaction while treating each electron independently. This means assuming that an electron labelled j, for example, can be described by the following effective Hamiltonian:

$$\hat{H}_{j,eff} = \frac{\hat{\mathbf{p}}_j^2}{2m_e} - \frac{Z_{eff,j}e^2}{4\pi\epsilon_0\hat{r}_j} + \delta V_j(\hat{r}_j), \quad (8.5)$$

where $Z_{eff,j}$ is a screened nuclear charge that the electron labeled as j experiences and $\delta V_j(\hat{r}_j)$ represents additional effects of other electrons that cannot be expressed

in the form of the Coulomb potential. In general, the value of $Z_{eff,j}$ and the detailed form of $\delta V_j(\hat{r}_j)$ should depend on the states of other electrons. This way, interdependency of different electrons are taken into consideration implicitly.

Care should be taken in devising an approximation as outlined above because the physical reality dictates that it is not possible to distinguish one electron from the other. For this reason, the labeling of electrons does not have genuine physical meaning and should be viewed as an intermediate step for calculating physical properties that are independent of the specific manner of the labeling. In addition, any many-electron state should be antisymmetric with respect to the exchange of any two electrons, which brings further complication. These issues will be addressed later in this chapter. For now, let us assume that an effective single electron state can be determined by solving the Schrödinger equation for the Hamiltonian of the type given by Eq. (8.5).

Because of the fact that the potential energy in Eq. (8.5) depends only on the magnitude operator of the position, $\hat{r}_j = |\hat{\mathbf{r}}_j|$, the effective Hamiltonian commutes with the angular momentum operators $\hat{\mathbf{L}}^2$ and $\hat{L}_z$. Therefore, within this approximation, the angular momentum quantum numbers l and m_l still serve as good quantum numbers. Another important fact is that the effective electron-nucleus Coulomb term of the potential remains dominant compared to the additional correction. This makes the principal quantum number of n determined for a hydrogen-like system a nearly good quantum number for classifying the eigenstates of the Hamiltonian. However, there is major difference from the hydrogen-like system in that the degeneracy of the energy for different values of l, which is a non-negative integer in the range of $[0, n-1]$ for a given quantum number n, gets lifted due to the additional term $\delta V_j(\hat{r}_j)$. Important qualitative trends and major definitions of terms are provided below.

Summary of Independent Electron Model

- For many-electron atoms, (n, l, m_l) serve as nearly good quantum numbers to represent effective spatial single electron states, which are also termed as **orbitals**.
- The collection of orbitals having the same value of n constitute a **shell**. Shells with $n = 1, 2, 3,$ and $4, \ldots$ are respectively denoted as K, L, M, $N, \ldots$.
- The energy of each orbital depends on both n and l, which are used for the labeling of different orbitals. Orbitals with $l = 0, 1, 2, 3, 4, \ldots$ are called $s, p, d, f, g, \cdots$, respectively.
- For each value of l, there are $2l + 1$ degenerate orbitals (in the absence of external field) with different values of m.
- For a given shell, orbitals with smaller values of l have lower energies than those with higher values of l. This is because electrons tend to have higher probability density near the nucleus for smaller value of l, which causes them to experience lower Coulomb potential energy.

Table 8.1 Numbers of orbitals and maximum numbers of electrons allowed for different types of orbitals

Orbital	s	p	d	f	g	h
Number of orbitals	1	3	5	7	9	11
Number of electrons	2	6	10	14	18	22

Given that all the single electron states have been identified in a given atom, one can then assign electrons to those states as if assigning one electron does not affect the other except for satisfying the symmetry rule for electrons as fermions. For this, first, it is important to note that *a state of an electron is defined by specifying both its orbital (spatial state) and the spin state*. Since electrons are fermions, only one electron can occupy one state. Since there are two spin states for each electron, this means that a single orbital can be occupied by two electrons at most.

8.2.2 Orbitals and Electronic Configuration

Since the number of orbitals for a given l is $(2l + 1)$, the maximum number of electrons allowed for orbitals with l are $2(2l + 1)$, as shown in Table 8.1.

Assuming that electrons for a given atom can be filled in one by one such that each of them occupies the lowest possible orbital, which is called *Aufbau principle* (building-up principle), it is possible to assign the relative order of orbitals.

The Order of Orbitals Based on Relative Energies

Given that all the orbitals with lower energies have already been filled, the following order of energies of orbitals has been established empirically.

– Increasing relative energy →

$1s$
$2s$ $2p$
$3s$ $3p$ $3d$
$4s$ $4p$ $4d$ $4f$
$5s$ $5p$ $5d$ $5f$
$6s$ $6p$ $6d$
$7s$ $7p$

In the above lists, each row represents different principal quantum number, and the orbitals on the right have higher energies than those on the left. Note that the intervals between different orbitals do not reflect the actual values of energy difference. Rather, the differences of energies become smaller as the principal quantum number increases.

The main factor that determines the relative energies are principal quantum numbers for s and p orbitals. However, for d and f orbitals, this is not the case. For example, nd orbitals have higher energies than $(n+1)s$ orbitals but lower energies than $(n+1)p$ orbitals. The atoms for which the d orbitals are partially filled correspond to transition metal elements. Also note that nf orbital has higher energy than $(n+2)s$ orbital but lower energy than $(n+1)d$ orbital. The atoms for which the f orbitals are partially filled are known as lanthanides and actinides. With these rules, it is now possible to determine all the ground state electron configurations for all the many-electron atoms. Some examples of ground state electronic configuration are shown below.

$$\begin{aligned}
&\text{Li}: 1s^2 2s^1 \\
&\text{C}: 1s^2 2s^2 2p^2 \\
&\text{Fe}: 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6
\end{aligned}$$

On the other hand, the following configurations correspond to excited state electronic configurations for the same atoms.

$$\begin{aligned}
&\text{Li}: 1s^1 2s^2;\ 1s^2 2p^1 \\
&\text{C}: 1s^1 2s^1 2p^3;\ 1s^1 2s^2 2p^1 3s^1 \\
&\text{Fe}: 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5 4p^1;\ 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^6 4p^1
\end{aligned}$$

8.2.3 Spin States

The total spin quantum number of two electrons occupying the same orbital is zero because it is possible only when their spins are opposite to each other. Likewise, when any type of orbitals is fully filled, the sum of all the spins of electrons is zero. Therefore, the total spin quantum number is zero for the following completely filled configurations: s^2, p^6, d^{10}, f^{14}, and g^{18}. For partially filled orbitals, there are various ways for the spins of electrons to be aligned with respect to each other. As a result, multiple spin states are possible.

Before detailed consideration of the spin states of partially filled orbitals, some mathematical account of the symmetry properties of many electron quantum states is needed. First of all, it is important to examine the properties of electrons as fermions. For many electron systems, this means that the total state should change its sign if two electrons are exchanged with each other. For example, consider the following multi-electron state:

$$|\Psi_{N_e}\rangle = |1, 2, \cdots, j, \cdots, k, \cdots, N_e\rangle, \tag{8.6}$$

where j denotes the label of each electron and the position of each label represents a single electron spin-orbit state that each electron is assigned to. For $|\Psi_N\rangle$ to be an acceptable N electron state, it should change its sign if electrons j and k are exchanged with each other as follows:

$$|\Psi_{N_e}\rangle = -|1, 2, \cdots, k, \cdots, j, \cdots, N_e\rangle. \tag{8.7}$$

For two electrons, this means that the spin states are antisymmetric when the orbital states are symmetric and vice versa.

For example, let us consider the s orbital for which there is only one orbital available for two electrons. The only possible two-electron orbital state in this case is

$$|\Phi_s(1,2)\rangle = |\phi_s(1)\rangle \otimes |\phi_s(2)\rangle = |\phi_s(1)\rangle|\phi_s(2)\rangle, \tag{8.8}$$

which is symmetric with respect to exchange of the two electrons because the order of two states in a direct product does not make any difference. The only two-electron spin state compatible with the above two-electron s orbital state is the following antisymmetric spin state called singlet:

$$|\chi_S(1,2)\rangle = \frac{1}{\sqrt{2}}\left(|\alpha(1)\rangle|\beta(2)\rangle - |\alpha(2)\rangle|\beta(1)\rangle\right), \tag{8.9}$$

which satisfies the antisymmetric property, $|\chi_S(1,2)\rangle = -|\chi_S(2,1)\rangle$. For this state, the total spin of electron is zero. Thus, the only acceptable two-electron spin-orbit state where two electrons occupy the same orbital is

$$|\Psi(1,2)\rangle = |\Phi_s(1,2)\rangle|\chi_S(1,2)\rangle, \tag{8.10}$$

which satisfies the antisymmetric property, $|\Psi(1,2)\rangle = -|\Psi(2,1)\rangle$ and has the total spin quantum number of $S = 0$.

On the other hand, one can also construct symmetric spin states. For two electrons, there are three such states as follows:

$$|\chi_T(1,2)\rangle = \begin{cases} |\alpha(1)\rangle|\alpha(2)\rangle \\ \frac{1}{\sqrt{2}}\left(|\alpha(1)\rangle|\beta(2)\rangle + |\beta(1)\rangle|\alpha(2)\rangle\right) \\ |\beta(1)\rangle|\beta(2)\rangle \end{cases} \tag{8.11}$$

These three states are collectively called triplet and have the total spin quantum number $S = 1$.

Let us now consider the case where two different orbitals $|\phi_a\rangle$ and $|\phi_b\rangle$ are available for two electrons. There are two possible ways for the two electrons occupy

these orbitals without violating the fact that they are indistinguishable as follows:

$$|\Phi_{sym}(1,2)\rangle = \frac{1}{\sqrt{2}}(|\phi_a(1)\rangle|\phi_b(2)\rangle + |\phi_a(2)\rangle|\phi_b(1)\rangle), \tag{8.12}$$

$$|\Phi_{asym}(1.2)\rangle = \frac{1}{\sqrt{2}}(|\phi_a(1)\rangle|\phi_b(2)\rangle - |\phi_a(2)\rangle|\phi_b(1)\rangle). \tag{8.13}$$

Then, the total spin-orbit states possible for the two electrons are as follows:

$$|\Psi_S(1,2)\rangle = |\Phi_{sym}(1,2)\rangle|\chi_S(1,2)\rangle, \tag{8.14}$$

$$|\Psi_T(1,2)\rangle = |\Phi_{asym}(1,2)\rangle|\chi_T(1,2)\rangle. \tag{8.15}$$

Note that both of above two states are antisymmetric with respect to the exchange of two electrons. These two states show that fully decoupled orbital and spin parts can be used to construct all possible and independent spin-orbit states for two electrons. However, it is not always the case for more than two electrons.

8.2.4 Energy Levels of Spin-Orbit States

While it is possible to determine relative energies of different configurations, a given electronic configuration does not provide full information on the energy of the many electron system because there are still many ways for the total angular momenta to be added up. For this, it is necessary to define all possible angular momentum quantum numbers that can be defined for many electron systems.

Angular Momentum Quantum Numbers for Many Electron System

Let us denote the orbital angular momentum vector and spin vector of the ith electron as $\mathbf{l}_i$ and $\mathbf{s}_i$, respectively. Different types of total angular momenta exist as described below.

- **Total angular momentum quantum number of a single electron** (j)—This represents the sum of orbital angular momentum and spin of an electron. Because $s = 1/2$, for a given value of l, there are only two possible values, $j = l + 1/2, l - 1/2$.
- **Total orbital angular momentum quantum number of all the electrons** (L)—This represents the quantum number for the sum of the orbital angular momenta of all the electrons.
- **Total spin quantum number of all the electrons** (S) -This represents the quantum number for the sum of the spins of all the electrons.

(continued)

- **Total angular momentum quantum number of all the electrons** (J)—This represents the sum of all the angular momenta of all the electrons.
- Each of the angular momentum quantum numbers listed above corresponds to the quantum numbers of the squares of corresponding angular momentum vector operators, $\hat{\mathbf{j}}$, $\hat{\mathbf{L}}$, $\hat{\mathbf{S}}$, and $\hat{\mathbf{J}}$. In other words, $\hbar^2 j(j+1)$, $\hbar^2 L(L+1)$, $\hbar^2 S(S+1)$, and $\hbar^2 J(J+1)$ are respectively eigenvalues of $\hat{\mathbf{j}}^2$, $\hat{\mathbf{L}}^2$, $\hat{\mathbf{S}}^2$, and $\hat{\mathbf{J}}^2$. With this understanding, for the determination of the quantum numbers, one has to consider only the vector nature of the orbital angular momentum operators. Therefore, we will omit the operator symbols whenever possible, and consider only the corresponding vectors in the consideration below.

Since the total angular momentum, namely, the sum of all orbital angular momenta and spins of all electrons, $\hat{\mathbf{J}}$, is a conserved quantity due to the spherical symmetry of the system, its quantum number J is always a good quantum number and can be included in any classification of the eigenstates of many-electron atoms. There are two ways to find out this quantum number. First, we can add all the orbital angular momentum vectors and spin vectors as follows:

$$\mathbf{L} = \sum_i \mathbf{l}_i, \tag{8.16}$$

$$\mathbf{S} = \sum_i \mathbf{s}_i. \tag{8.17}$$

Then, the total sum of the angular momentum and the spin vectors is given by

$$\mathbf{J} = \mathbf{L} + \mathbf{S}. \tag{8.18}$$

This is called LS-coupling or Russell-Saunders coupling scheme, and works well when spin-orbit coupling of an individual electron is weak as in most light atoms. This is not the case for heavy atoms for which the large nuclear charge creates strong spin-orbit coupling especially for those core electrons. For this case, the following individual **j**'s serve as better quantum numbers.

$$\mathbf{j}_i = \mathbf{l}_i + \mathbf{s}_i. \tag{8.19}$$

The total angular momentum vector in this case is given by

$$\mathbf{J} = \sum_i \mathbf{j}_i. \tag{8.20}$$

This is called jj-coupling scheme, which becomes complicated as the number of electrons increases.

8.2.5 Examples of Energy Levels Based on LS-Coupling Scheme

Within the LS-coupling scheme, one only needs to specify L, S, and J values. The electronic term symbols introduced in Chap. 6 can be used for this purpose. Let us consider the simplest example, two electrons in helium, He. The ground electronic configuration of He is $1s^2$. Since this corresponds to a completely filled orbital, $L = 0$ and $S = 0$. Therefore, $J = 0$ as well. This configuration has only one term, $^1\mathrm{S}_0$.

Next, let us consider an excited state configuration of He given by $1s^12p^1$. For this, only $L = 1$ is possible. On the other hand, for the total spin, $S = 0, 1$ are possible. Since two electrons occupy two different orbitals, either $S = 0$ or $S = 1$ is acceptable. When $S = 0$, only $J = 1$ is possible. The term symbol for this case is $^1\mathrm{P}_1$. When $S = 1$, three values of $J = 0, 1, 2$ are possible. Term symbols for these cases are as follows: $^3\mathrm{P}_0$, $^3\mathrm{P}_1$, and $^3\mathrm{P}_2$.

For Li, which has three electrons, the ground electronic configuration is $1s^22s^1$. This is effectively one electron system since two electrons are in a completely filled orbital. The orbital angular momentum quantum number of this electron is $L = 0$, since it is in s orbital. For this one electron, $S = 1/2$. The only possible combination of this spin and the orbital angular momentum $L = 0$ is such that $J = 1/2$. Therefore, the term symbol for this is $^2\mathrm{S}_{1/2}$.

For Be, there are four electrons. However, the ground electronic configuration is $1s^22s^2$, where two s orbitals are completely filled. As in the case of He, $L = 0$, $S = 0$, and $J = 0$ for this configuration. Therefore, the term symbol for this is $^1\mathrm{S}_0$.

For boron, B, there are five electrons. Out of these, four electrons completely fill in $1s$ and $2s$ orbitals and only one electron occupies a $2p$ orbital. Therefore, the ground electronic configuration is $1s^22s^22p^1$. For this, $L = 1$ and $S = 1/2$. Possible values of J in this case are $3/2$ and $1/2$. Therefore, there are two terms, $^2\mathrm{P}_{1/2}$ and $^2\mathrm{P}_{3/2}$.

Determination of term symbols so far have been simple because orbitals are completely filled or occupied with single electrons. When there are more than one electrons occupying the same orbital, care should be taken. This is the case for carbon, C, for which the ground electronic configuration is $1s^22s^22p^2$. Although all the electrons are equivalent for a given atom, for practical reasons, it is assumed that electrons assigned to different orbitals have unique labels and are thus nonequivalent. This is certainly an approximation but a useful one. Within this approximation, electrons in the filled orbitals need not be considered because their net orbital and spin angular momenta are zero. Thus, two electrons in unfilled p orbitals only need to be considered.

Table 8.2 Possible combinations of L and S and term symbols for two equivalent p electrons

L	S	J	Term Symbols
2	0	2	$^1D_2$
1	1	2,1,0	$^3P_2,\ ^3P_1,\ ^3P_0$
0	0	0	$^1S_0$

For the two electrons occupying $2p$ orbitals, the total angular momentum quantum numbers of $L = 2, 1, 0$ are possible. For the total spin, two quantum numbers for the total spin $S = 0, 1$ are possible. Due to the symmetry requirement, not all the three values of L can be combined with the two values of S. Instead, only the combinations given in Table 8.2 are possible.

A simple way of finding term symbols without going through full angular momentum calculation as introduced by Landau and Lifshitz [7] is described below. Note that each electron has $l = 1$ and $s = 1/2$. Therefore, there are six possible combinations for the sets of (l_z, s_z) as follows:

$$a : \left(1, \frac{1}{2}\right) \qquad b : \left(0, \frac{1}{2}\right) \qquad c : \left(-1, \frac{1}{2}\right)$$
$$a' : \left(1, -\frac{1}{2}\right) \qquad b' : \left(0, -\frac{1}{2}\right) \qquad c' : \left(-1, -\frac{1}{2}\right)$$

The set of (L_z, S_z) can be found by summing two out of the above six states. In enumerating all possible sums, one needs to consider only two rules. First, the sum of the same set is not allowed because it is not possible to make it antisymmetric with respect to the exchange of two electrons. Second, we only need to consider nonnegative values of L_z and S_z because the numbers of positive and negative values are always the same.

The resulting list of all possible distinctive combinations with non-negative values of L_z and S_z are as follows:

$$\begin{array}{lll} a + a' : (2, 0) & a + b : (1, 1) & a + c : (0, 1) \\ & a + b' : (1, 0) & a + c' : (0, 0) \\ & a' + b : (1, 0) & a' + c : (0, 0) \\ & & b + b' : (0, 0)\ , \end{array}$$

where each column corresponds to a different value of L_z. For each column, those with higher value of S_z appear in upper rows. Based on the above combinations, it is possible to deduce all possible term symbols.

First, the presence of $(2, 0)$ means that there has to be a state with $L = 2$ and $S = 0$. This also means that there have to be two additional combinations: $(1, 0)$ and $(0, 0)$, which correspond to different possible nonnegative values of L_z for $L = 2$ and $S = 0$. Thus, we have found three possible combinations of L_z and S_z corresponding to the term ^{1}D. Removing these combinations from the list of

combinations shown above, we are now left with the following combinations:

$$\begin{array}{ll} (1,1) & (0,1) \\ (1,0) & (0,0) \\ & (0,0) \end{array}$$

Note that the origin of each of the above combinations has been left out because it does not matter in identifying term symbols. In the above combinations, the presence of (1, 1) implies that there has to be a state with $L = 1$ and $S = 1$. This implies the existence of the following combinations: $L_z = 1$, $S_z = 1, 0$; $L_z = 0$, $S_z = 1, 0$. All of these correspond to (1, 1), $(1, 0)$, (0, 1), $(0, 0)$, which constitute the term ^{3}P. Subtracting these from the above combinations, we are now left with the following single combination: $(0, 0)$. This single combination implies that $L = 0$ and $S = 0$, which corresponds to the term ^{1}S. Thus, we have identified all three terms that appear in Table 8.2, ^{1}D, ^{3}P, and ^{1}S. For each case, all possible values of J can be obtained following the rules for the addition of angular momentum quantum numbers explained before.

The approach described above can be extended to the case of three electrons. Consider the configuration p^3. All the possible combinations are as follows:

$$\begin{array}{lll} a + a' + b : (2, \frac{1}{2}) & a + a' + c : (1, \frac{1}{2}) & a + b + c : (0, \frac{3}{2}) \\ & a + b + b' : (1, \frac{1}{2}) & a + b' + c : (0, \frac{1}{2}) \\ & & a + b + c' : (0, \frac{1}{2}) \\ & & a' + b + c : (0, \frac{1}{2}) \end{array}$$

From the above combinations, following a similar procedure, we can find out the following term symbols: $^4\mathrm{S}_{\frac{3}{2}}$, $^2\mathrm{P}_{\frac{3}{2}}$, $^2\mathrm{P}_{\frac{1}{2}}$, $^2\mathrm{D}_{\frac{5}{2}}$, and $^2\mathrm{D}_{\frac{3}{2}}$.

Having identified all possible terms, the next step is to determine the relative energy levels. There are three well known rules [31] for this. First, two rules by Hund prescribe relative energies based on the values of L and S as described below.

Hund's Rules

According to Hund, relative energies of different terms can be determined based on the following two rules:

(i) Of all the terms arising from the same electronic configuration, those with the highest multiplicity (largest value of S) lie lowest in energy.

(continued)

(ii) Of all the terms with the same value of S arising from the same electronic configuration, the lowest is that with the highest value of L.

The justification for (i) is that the states with the largest multiplicity have the lowest electron-electron repulsion. The justification for (ii) is that the highest L states can penetrate toward the nucleus more easily, and thus experiences larger effective charge and thus lower energy.

Of the terms with the same values of L and S that originate from the same electronic configuration, Lande's interval rule as described below then prescribes relative energies depending on the value of J.

Lande's Interval Rule

For less than half-filled orbitals, smaller J has lower energy (normal case). For more than half filled orbitals, larger J has lower energy (inverted case). This is due to the spin-orbit coupling, which results in the following form of energy difference between different values of J:

$$E_J - E_{J-1} = AJ. \tag{8.21}$$

A is positive for *normal case* and is negative for *inverted case*. The above prescription leaves the case with exactly half-filled case undetermined, for which the rule for normal case seems to work in general.

8.2.6 *Atomic Spectroscopy: Selection Rules and Simple Examples*

Atomic spectroscopy results from the transition between many electron states due to interaction with a photon. The Russell-Saunders coupling scheme and the corresponding electronic terms can be used for fairly accurate description of the spectroscopy of light atoms and the relevant selection rules [31] are easy to understand.

Selection Rules for General Many-Electron Atoms

The general selection rules governing the transition between two electronic states of many-electron atoms, $(L', S', J') \rightarrow (L'', S'', J'')$, are as follows.

$$\Delta S = 0 \tag{8.22}$$

$$\Delta L = \begin{cases} \pm 1, 0 & \text{if } L' \neq 0 \\ 1 & \text{if } L' = 0 \end{cases} \tag{8.23}$$

$$\Delta J = 0, \pm 1 \text{ (no } 0 \leftrightarrow 0 \text{ transition)} \tag{8.24}$$

The fact that the total spin of electrons does not change, Eq. (8.22), results from the fact that electrons interact only with the electric field component of the light which does not affect the spins of electrons. Of course, this selection rule can be broken if there is significant spin-orbit coupling. The selection rule for ΔL, Eq. (8.23), results from the fact that the sum of the total angular momentum of electrons and the spin of photon, which is one, should remain conserved. The selection rule concerning ΔJ is an outcome of those for ΔS and ΔL.

Another important selection rule that is fundamental but can be overlooked easily is the Laporte's rule as described below.

Laporte's Rule

The transition in atomic spectroscopy is allowed only between terms originating from two different electronic configurations that satisfies the following condition:

$$\sum_i l_i \text{ : even} \leftrightarrow \text{odd} \tag{8.25}$$

This rule results from the fact that the dipole operator involved in the interaction with the light has odd inversion symmetry and thus can connect only two electronic configurations with different inversion symmetries, which are determined by the sum of all individual angular momentum quantum numbers. As a result of this rule, transitions between terms coming from the same electronic configurations are not allowed.

As the simple examples of the atomic spectroscopy, some major results for the spectroscopy of alkali metal and alkaline earth metal atoms [31] are briefly described below.

Alkali Metals The emission spectra of alkali metal atoms consist of four series: S (sharp, $s \rightarrow p$), P (principal, $p \rightarrow s$), D (diffuse, $d \rightarrow p$), and F (fundamental, $f \rightarrow d$). Only one electron is involved in these transitions and the selection rules are similar to those for hydrogen atoms. That is, Δn is unrestricted, $\Delta l = \pm 1$, and $\Delta J = 0, \pm 1$ except that $J = 0 \leftrightarrow J = 0$ is forbidden. Note that $\Delta J = 0$ can be consistent with $\Delta l = \pm 1$ due to the interplay of the spin state except when $J = 0$. The principal series in the sodium atom result from the transitions, $n\ ^2\mathrm{P}_{1/2} \rightarrow 3\ ^2\mathrm{S}_{1/2}$ and $n\ ^2\mathrm{P}_{3/2} \rightarrow 3\ ^2\mathrm{S}_{1/2}$, where $n \geq 3$. The lowest of these are called sodium D lines, which have the wavelengths of 589.592 nm and 588.995 nm.

Helium and Alkaline Earth Metal Atoms In the ground state where the two electrons are in the same s-type orbital, the total spin state is singlet. However, when one electron is excited and thus there are two nonequivalent electrons, both singlet and triplet states are possible. However, the triplet excited states are not optically accessible from the ground state because of the following selection rules: $\Delta S = 0$. That is, only singlet-singlet and triplet-triplet transitions, with $\Delta l = \pm 1$ for the promoted electron, are allowed.

8.3 Case Study of Helium Atom

This section provides a detailed mathematical description of independent electron model and then more advanced self-consistent field (SCF) approximation for the case of helium atom.

8.3.1 Hamiltonian and Schrödinger Equation

The full Hamiltonian for a helium atom is given by

$$\begin{aligned}\hat{H}_{\mathrm{He}} = &-\frac{\hbar^2}{2m_c}\nabla_c^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 \\ &-\frac{2e^2}{4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{R}_c|} - \frac{2e^2}{4\pi\epsilon_0|\mathbf{r}_2 - \mathbf{R}_c|} + \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|}.\end{aligned} \tag{8.26}$$

Working in terms of the center of mass and relative coordinates in this case is mathematically complicated. Thus, using the fact that $m_c >> m_e$, let us assume that the nucleus is fixed at the origin and that the kinetic energy of the nucleus can be ignored. With this assumption, the following Hamiltonian for the electrons in helium atom can be used:

$$\hat{H}_{\mathrm{He},el} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}, \tag{8.27}$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. Then, let us introduce $\psi_{\text{He},e}(\mathbf{r}_1, \mathbf{r}_2)$ as the eigenfunction of the above Hamiltonian that satisfies the following time independent Schrödinger equation:

$$\hat{H}_{\text{He},el}\psi_{\text{He},e}(\mathbf{r}_1, \mathbf{r}_2) = E\psi_{\text{He},e}(\mathbf{r}_1, \mathbf{r}_2). \tag{8.28}$$

The two-electron wave function $\psi_{\text{He},e}(\mathbf{r}_1, \mathbf{r}_2)$ is defined in the six dimensional space of the two electron coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$, and provides full information on the electrons within the helium atom under the assumption that the nuclear kinetic energy, the contribution of which is extremely small, can be ignored. Unfortunately, no exact solution has been found even for this simplest example of the multi-electron system. Thus, one has to rely on approximation methods.

8.3.2 Independent Electron Model with Variational Optimization of Effective Charge

Let us consider the simplest independent electron model that assumes $\psi_{\text{He},e}(\mathbf{r}_1, \mathbf{r}_2)$ as the product of two eigenfunctions for hydrogen-like systems. For this, it is useful to divide the Hamiltonian as follows [1]:

$$\hat{H}_{\text{He},el} = \hat{H}_{\text{H},Z=2}(1) + \hat{H}_{\text{H},Z=2}(2) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}}, \tag{8.29}$$

where $\hat{H}_{H,Z=2}(1)$ and $\hat{H}_{H,Z=2}(2)$ represent the Hamiltonian of a single electrons 1 and 2 around a nucleus of charge $Z = 2$ at the origin, respectively, and are expressed as

$$\hat{H}_{\text{H},Z=2}(j) = -\frac{\hbar^2}{2m_e}\nabla_j^2 - \frac{2e^2}{4\pi\epsilon_0}\frac{1}{r_j}\ , \ j = 1, 2 \tag{8.30}$$

On the other hand, the Hamiltonian of a single electron interacting with a nucleus with charge Z at the origin is

$$\hat{H}_{\text{H},Z} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}. \tag{8.31}$$

Eigenvalues for the above Hamiltonian can be expressed as

$$E_n = -\frac{Z^2\hbar^2}{2m_e a_0^2}\frac{1}{n^2}\ , \ \text{for } n = 1, 2, 3, \cdots \tag{8.32}$$

where a_0 is the Bohr radius (the effective radius of the hydrogen atom) defined as

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}. \tag{8.33}$$

Similarly, the eigenfunction of $\hat{H}_{H,Z}$, which depends on the three quantum numbers as detailed in Chap. 6, is given by

$$\psi_{n,l,m_l}(r,\theta,\phi) = R_{nl}(r)Y_l^{m_l}(\theta,\phi), \tag{8.34}$$

where $Y_l^{m_l}(\theta,\phi)$ is the spherical harmonics and $R_{nl}(r)$ is the radial function defined as

$$R_{nl}(r) = \left(\frac{(n-l-1)!}{2n[(n+l)!]^3}\right)^{1/2}\left(\frac{2Z}{na_0}\right)^{l+\frac{3}{2}} r^l L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_0}\right)e^{-Zr/(na_0)}. \tag{8.35}$$

In the above expression, $L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_0}\right)$ is an associated Laguerre polynomial as defined in Chap. 6.

Now let us consider the following trial wave function:

$$\phi_0(\mathbf{r}_1,\mathbf{r}_2) = \psi_{1s}(Z,r_1)\psi_{1s}(Z,r_2)\ . \tag{8.36}$$

where $\psi_{1s}(Z,r)$ is the $1s$ eigenfunction for the hydrogen-like system with nuclear charge Z, a parameter to be determined later, and is given by

$$\psi_{1s}(Z,r) = \psi_{100}(\mathbf{r}) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0}. \tag{8.37}$$

Then, it is easy to show that

$$\begin{aligned}\hat{H}_{\mathrm{H},Z=2}(j)\psi_{1s}(Z,r_j) &= \left(-\frac{\hbar^2}{2m_e}\nabla_j^2 - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_j} - \frac{(2-Z)e^2}{4\pi\epsilon_0}\frac{1}{r_j}\right)\psi_{1s}(Z,r_j)\\ &= \left(-\frac{Z^2\hbar^2}{2m_e a_0^2} - \frac{(2-Z)e^2}{4\pi\epsilon_0}\frac{1}{r_j}\right)\psi_{1s}(Z,r_j).\end{aligned} \tag{8.38}$$

Therefore, application of the Hamiltonian, Eq. (8.29), to the trial wavefunction $\phi_0(\mathbf{r}_1,\mathbf{r}_2)$ results in

$$\hat{H}_{\mathrm{He},el}\phi_0(\mathbf{r}_1,\mathbf{r}_2) = \left(-\frac{Z^2\hbar^2}{m_e a_0^2} - \frac{(2-Z)e^2}{4\pi\epsilon_0}\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \frac{e^2}{4\pi\epsilon_0 r_{12}}\right)\phi_0(\mathbf{r}_1,\mathbf{r}_2). \tag{8.39}$$

As is clear from Eq. (8.39), $\phi_0(\mathbf{r}_1, \mathbf{r}_2)$ cannot be an eigenfunction $\hat{H}_{\mathrm{He},e}$ even when $Z = 2$ because of the last electron-electron repulsion term. In fact, $Z = 2$ is not expected to be the best choice considering that the electron-electron repulsion term causes partial screening of the nuclear charge. According to the variational theorem as described in Chap. 7, the best choice of Z is the one that minimizes the expectation value of the Hamiltonian. Therefore, let us first calculate the following expectation value:

$$
\begin{aligned}
E_\phi &= \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_0(\mathbf{r}_1, \mathbf{r}_2) \hat{H}_{\mathrm{He},e} \phi_0(\mathbf{r}_1, \mathbf{r}_2) \\
&= -\frac{Z^2 \hbar^2}{m_e a_0^2} - \frac{2(2-Z)e^2}{4\pi\epsilon_0} \int d\mathbf{r}\, \psi_{1s}(Z, \mathbf{r}) \frac{1}{r} \psi_{1s}(Z, \mathbf{r}) \\
&\quad + \frac{e^2}{4\pi\epsilon_0} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_0(\mathbf{r}_1, \mathbf{r}_2) \frac{1}{r_{12}} \phi_0(\mathbf{r}_1, \mathbf{r}_2).
\end{aligned} \tag{8.40}
$$

In the above expression, the two integrals can be calculated explicitly as follows:

$$
\int d\mathbf{r}\, \psi_{1s}(Z, \mathbf{r}) \frac{1}{r} \psi_{1s}(Z, \mathbf{r}) = \frac{Z}{a_0}, \tag{8.41}
$$

$$
\int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_0(\mathbf{r}_1, \mathbf{r}_2) \frac{1}{r_{12}} \phi_0(\mathbf{r}_1, \mathbf{r}_2) = \frac{5Z}{8a_0}. \tag{8.42}
$$

Thus, employing the above expressions and the definition of a_0 given by Eq. (8.33), one can express the expectation value E_ϕ as follows [1]:

$$
E_\phi = -\frac{\hbar^2}{m_e a_0^2} \left\{ Z^2 + 2Z(2-Z) - \frac{5}{8} Z \right\} = \frac{\hbar^2}{m_e a_0^2} \left\{ Z^2 - \frac{27Z}{8} \right\}. \tag{8.43}
$$

Equation (8.43) shows that the expectation value of the Hamiltonian is a quadratic function of Z. Thus, it becomes minimum for the value of Z that satisfies the following condition:

$$
\frac{\partial E}{\partial Z} = \frac{\hbar^2}{m_e a_0^2} \left\{ 2Z - \frac{27}{8} \right\} = 0\,, \tag{8.44}
$$

which results in $Z_{opt} = 27/16$. This implies that the electron-electron repulsion can be seen as screening the charge of the nucleus by $5/16$. Using this value in Eq. (8.43), we find that the best estimate for the ground state electronic energy of the helium atom within the present approximation is

$$
E_{min} = -\left(\frac{27}{16} \right)^2 \frac{\hbar^2}{m_e a_0^2} = -2.8477 \frac{\hbar^2}{m_e a_0^2}. \tag{8.45}
$$

8.3.3 Self Consistent Field (SCF) Approximation for Helium

As a preliminary step for a general description of SCF approximations, let us use the helium atom as an example and go through approximations involved in this approach in more detail [1]. In order to clarify the main ideas in this approach, let us now use the atomic and Gauss units where $\hbar = m_e = a_0 = e = 1$. Then, the expression for the electronic Hamiltonian of the helium atom can be expressed as

$$\hat{H}_{\mathrm{He},el} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}. \tag{8.46}$$

Let us assume that the two electron wavefunction can once again be expressed as a product of single electron wavefunctions as follows: $\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)$, which are assumed to be normalized. Then,

$$E[\psi_1.\psi_2] = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \psi^*(\mathbf{r}_1, \mathbf{r}_2)\hat{H}\psi(\mathbf{r}_1, \mathbf{r}_2) = I_1[\psi_1] + I_2[\psi_2] + J_{12}[\psi_1, \psi_2], \tag{8.47}$$

where the square brackets imply that they are functionals of the functions within them. Thus,

$$I_1[\psi_1] = \int d\mathbf{r}_1 \psi_1^*(\mathbf{r}_1)\left(-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1}\right)\psi_1(\mathbf{r}_1), \tag{8.48}$$

$$I_2[\psi_2] = \int d\mathbf{r}_2 \psi_2^*(\mathbf{r}_2)\left(-\frac{1}{2}\nabla_2^2 - \frac{2}{r_2}\right)\psi_2(\mathbf{r}_2), \tag{8.49}$$

$$J_{12}[\psi_1, \psi_2] = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \psi_1^*(\mathbf{r}_1)\psi_2^*(\mathbf{r}_2)\frac{1}{r_{12}}\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2). \tag{8.50}$$

Let us also define

$$V_{12}^{eff}(\mathbf{r}_1)[\psi_2] = \int d\mathbf{r}_2 \psi_2^*(\mathbf{r}_2)\frac{1}{r_{12}}\psi_2(\mathbf{r}_2), \tag{8.51}$$

which is an effective potential energy that electron 1 experiences due to electron 2 and is thus the functional of $\psi_2(\mathbf{r})$. Then,

$$J_{12}[\psi_1, \psi_2] = \int d\mathbf{r}_1\ \psi_1^*(\mathbf{r}_1)V_{12}^{eff}(\mathbf{r}_1)[\psi_2]\psi_1(\mathbf{r}_1). \tag{8.52}$$

Alternatively, we can also define

$$V_{21}^{eff}(\mathbf{r}_2)[\psi_1] = \int d\mathbf{r}_1 \psi_1^*(\mathbf{r}_1)\frac{1}{r_{12}}\psi_1(\mathbf{r}_1), \tag{8.53}$$

which is an effective potential energy that electron 2 experiences due to electron 1 and is also a functional of $\psi(\mathbf{r}_1)$. Then,

$$J_{12}[\psi_1, \psi_2] = \int d\mathbf{r}_2\ \psi_2^*(\mathbf{r}_2) V_{21}^{eff}(\mathbf{r}_2)[\psi_1]\psi_2(\mathbf{r}_2). \tag{8.54}$$

Finally, let us introduce an effective total potential for electron 1,

$$V_1(\mathbf{r}_1)[\psi_2] = -\frac{2}{r_1} + V_{12}^{eff}(\mathbf{r}_1)[\psi_2], \tag{8.55}$$

and define an effective one-electron Hamiltonian for particle 1,

$$\hat{H}_1[\psi_2] = -\frac{1}{2}\nabla_1^2 + \hat{V}_1(\mathbf{r}_1)[\psi_2]. \tag{8.56}$$

Then, we can define an effective one-electron wavefunction that satisfies the following Schrödinger equation:

$$\hat{H}_1[\psi_2]\psi_1(\mathbf{r}_1) = \mathcal{E}_1[\psi_1, \psi_2]\psi_1(\mathbf{r}_1), \tag{8.57}$$

where the fact that $\mathcal{E}_1[\psi_1, \psi_2]$ is a functional of both ψ_1 and ψ_2 according to the following identity has been used.

$$\mathcal{E}_1[\psi_1, \psi_2] = \int d\mathbf{r}_1 \psi_1^*(\mathbf{r}_1)\hat{H}_1[\psi_2]\psi_1(\mathbf{r}_1) = I_1[\psi_1] + J_{12}[\psi_1, \psi_2]. \tag{8.58}$$

Similarly, we can also introduce an effective total potential for electron 2 as follows:

$$V_2(\mathbf{r}_2)[\psi_1] = -\frac{2}{r_2} + V_{21}^{eff}(\mathbf{r}_2)[\psi_1], \tag{8.59}$$

and define the Hamiltonian and effective one-electron Schrödinger equation for the wavefunction for particle 2 as follows:

$$\hat{H}_2[\psi_1] = -\frac{1}{2}\nabla_2^2 + \hat{V}_2(\mathbf{r}_2)[\psi_1], \tag{8.60}$$

$$\hat{H}_2[\psi_1]\psi_2(\mathbf{r}_2) = \mathcal{E}_2[\psi_1, \psi_2]\psi_2(\mathbf{r}_2). \tag{8.61}$$

Then,

$$\mathcal{E}_2[\psi_1, \psi_2] = \int d\mathbf{r}_2 \psi_2^*(\mathbf{r}_2)\hat{H}_2\psi_2(\mathbf{r}_1) = I_2[\psi_2] + J_{12}[\psi_1, \psi_2]. \tag{8.62}$$

Equations (8.57) and (8.61) are effective single electron equations, and constitute the major equations to be solved. It is important to note that these are different from conventional one particle Schrödinger equations because the terms constituting

the Hamiltonian depend on the choice of as yet undetermined wavefunction. Thus, these have to be solved in a self consistent manner. For example, one can start from the first guess of the wavefunctions and then continue iterations. One important point to recognize in conducting such iterations is that the two effective one-electron wavefunctions are not independent but are coupled together as follows:

$$\psi_2^{(0)}(\mathbf{r}_2) \rightarrow V_{12}^{eff}(\mathbf{r}_1)[\psi_2^{(0)}] \rightarrow \hat{H}_1[\psi_2^{(0)}] \rightarrow \psi_1^{(1)}(\mathbf{r}_1) \rightarrow \cdots \tag{8.63}$$

$$\psi_1^{(0)}(\mathbf{r}_1) \rightarrow V_{21}^{eff}(\mathbf{r}_2)[\psi_1^{(0)}] \rightarrow \hat{H}_2[\psi_1^{(0)}] \rightarrow \psi_2^{(1)}(\mathbf{r}_2) \rightarrow \cdots \tag{8.64}$$

This procedure can continue until $\mathcal{E}_1$ and $\mathcal{E}_2$ being determined converge. Note that the total energy is not equal to the sum of orbital energies. Rather, it is given by

$$E = I_1 + I_2 + J_{12} = \mathcal{E}_1 + \mathcal{E}_2 - J_{12}, \tag{8.65}$$

where the last term accounts for the electron-electron repulsion that is double counted when the two orbital energies are added up.

The SCF approximation described above is known as the Hartree approximation and in general produces a better solution than simply assuming an eigenfunction for a hydrogen-like system for the single electron wavefunction. Of course, the actual performance of this approach depends on the choice of basis functions used for expanding the single electron wavefunction.

One important issue that was not considered so far is the symmetry requirement for the final solution since the total two-electron wavefunction should be antisymmetric with respect to the exchange of the two electrons. Assuming that the two electrons occupy the same orbital, ensuring such symmetry requirement is easy. One simply needs to assume that $\psi_1^{(k)}(\mathbf{r}) = \psi_2^{(k)}(\mathbf{r})$ throughout the iteration procedure and use the singlet spin state. However, if more than two electrons and one orbital are involved, such procedure can be cumbersome. Thus, it is best to devise a method that satisfies the symmetry requirement.

8.4 Self Consistent Field (SCF) Approximation for Many Electron Atoms

Consider many electron atoms or ions with nuclear charge of Z. The classical Hamiltonian for this system in atomic units is

$$\begin{aligned} H_{el} &= \frac{1}{2}\sum_{j=1}^{N_e} \mathbf{p}_j^2 - \sum_{j=1}^{N_e} \frac{Z}{r_j} + \frac{1}{2}\sum_{j=1}^{N_e}\sum_{k\neq j} \frac{1}{r_{jk}} \\ &= \sum_{j=1}^{N_e} h_j + \frac{1}{2}\sum_{j=1}^{N_e}\sum_{k\neq j} \frac{1}{r_{jk}}, \end{aligned} \tag{8.66}$$

where the second line defines h_j, the single electron term of the Hamiltonian representing its kinetic energy and potential energy with the nucleus, and $r_{jk} = |\mathbf{r}_j - \mathbf{r}_k|$ with $\mathbf{r}_j$ and $\mathbf{r}_k$ respectively denoting the coordinates of electrons j and k. The corresponding quantum mechanical Hamiltonian operator can be expressed as

$$\hat{H}_{el} = \sum_{j=1}^{N_e} \hat{h}_j + \frac{1}{2} \sum_{j=1}^{N_e} \sum_{k \neq j} \frac{1}{\hat{r}_{jk}}, \tag{8.67}$$

where

$$\hat{h}_j = \frac{\hat{p}_j^2}{2} - \frac{Z}{\hat{r}_j}, \tag{8.68}$$

$$\frac{1}{\hat{r}_{jk}} = \frac{1}{|\hat{\mathbf{r}}_j - \hat{\mathbf{r}}_k|}. \tag{8.69}$$

Let us denote an N_e-electron eigenstate of $\hat{H}_{el}$ with eigenvalue E_{N_e} as $|\Psi_{N_e}\rangle$.[1] Thus,

$$\hat{H}_{el} |\Psi_{N_e}\rangle = E_{N_e} |\Psi_{N_e}\rangle. \tag{8.70}$$

It is straightforward to extend the independent electron model and the SCF approximation that have been detailed for the helium atom to find approximations for the above many-electron Schrödinger equation. In the description below, we go back to the Dirac notation for more compact presentation of formulation.

8.4.1 Hartree Approximation

The Hartree approximation can easily be extended to the general n electron state. For this, let us introduce single electron states, $|\psi_1(1)\rangle, \cdots, |\psi_{N_e}(N_e)\rangle$, where ψ_k denotes the kth spin orbit state and the argument inside of this is the label of each electron. Thus, each of the single electron state represents the electron 1 in state ψ_1, the electron 2 in state $|\psi_2\rangle$, and so on. Let us also assume for now that the N_e-electron state can be expressed as the direct product of the single electron states as follows:[2]

$$\begin{aligned} |\Psi_{N_e}\rangle &= |\psi_1(1)\rangle \otimes |\psi_2(2)\rangle \otimes \cdots \otimes |\psi_{N_e}(N_e)\rangle \\ &= |\psi_1(1)\rangle |\psi_2(2)\rangle \cdots |\psi_{N_e}(N_e)\rangle. \end{aligned} \tag{8.71}$$

[1] Although there are many eigenstates, which all have to be labeled with appropriate indices, we do not consider them now but focus only on one of them, particularly, the ground electronic state here.

[2] Apparently, this state is not consistent with the fact that all electrons are equivalent let alone it does not satisfy the Pauli exclusion principle.

Within this approximation, following a similar procedure as in the helium atom, the Hartree approximation for the total energy can be expressed as follows:

$$
\begin{aligned}
& E_{N_e}[\psi_1, \cdots, \psi_{N_e}] \\
&= \langle \psi_1(1)| \cdots \langle \psi_{N_e}(N_e)| \left(\sum_{j=1}^{N_e} \hat{h}_j + \frac{1}{2} \sum_{j=1}^{N_e} \sum_{k \neq j} \frac{1}{\hat{r}_{jk}} \right) |\psi_1(1)\rangle \cdots |\psi_{N_e}(N_e)\rangle \\
&= \sum_{j=1}^{N_e} \left(I_j[\psi_j] + \frac{1}{2} \sum_{j \neq k} J_{jk}[\psi_j, \psi_k] \right),
\end{aligned}
\tag{8.72}
$$

where

$$
I_j[\psi_j] = \langle \psi_j(j)|\hat{h}_j|\psi_j(j)\rangle, \tag{8.73}
$$

$$
J_{jk}[\psi_j, \psi_k] = \langle \psi_j(j)|\langle \psi_k(k)|\frac{1}{\hat{r}_{jk}}|\psi_j(j)\rangle|\psi_k(k)\rangle. \tag{8.74}
$$

In above expressions, those in the square brackets denote their functional dependences. In other words, E_{N_e} depends on the choice of all of $|\psi_1(1)\rangle, \cdots, |\psi_{N_e}(N_e)\rangle$, I_j only on the choice of $|\psi_j(j)\rangle$, and J_{jk} on the choice of the two states $|\psi_j(j)\rangle$ and $|\psi_k(k)\rangle$. From now on, for notational conveniences, these dependences will be omitted.

On the other hand, let us introduce the following effective one-electron Hamiltonian operator:

$$
\hat{H}_j = \hat{h}_j + \sum_{k \neq j} J_{jk} |\psi_j(j)\rangle\langle\psi_j(j)|, \tag{8.75}
$$

where the second term represents the potential of electron j due to others and is based on the assumption that each of electron j is in the state $|\psi_j(j)\rangle$, which is yet undetermined. Now, let us assume that $|\psi_j(j)\rangle$ can be determined to be the eigenstate of $\hat{H}_j$ with eigenvalue $\mathcal{E}_j$ as follows:

$$
\hat{H}_j|\psi_j(j)\rangle = \left(\hat{h}_j + \sum_{k \neq j} J_{jk} \right) |\psi_j(j)\rangle = \mathcal{E}_j|\psi_j(j)\rangle. \tag{8.76}
$$

Then, taking the inner product of the above equation with $\langle\psi_j(j)|$, we obtain the following expression for the energy of electron j:

$$
\mathcal{E}_j = I_j + \sum_{k \neq j} J_{jk}, \tag{8.77}
$$

where the definition of Eq. (8.73) has been used. The total energy of the N_e-electron system, Eq. (8.72), can thus be expressed using the above definition of single electron energy as follows:

$$E_{N_e} = \sum_{j=1}^{N_e} \mathcal{E}_j - \frac{1}{2} \sum_{j=1}^{N_e} \sum_{k \neq j} J_{jk}. \tag{8.78}$$

Equations (8.76)–(8.78) serve as the formal framework for the iteration procedure in the Hartree approximation, and one can continue the following procedure until convergence in E_{N_e} is reached.

1. Choose the initial guess states for $|\psi_1^{(0)}(1)\rangle, \cdots, |\psi_{N_e}^{(0)}(N_e)\rangle$.
2. Determine $\hat{h}_j$ and J_{jk} using the states determined in step (1).
3. Solve the one electron Schrödinger equation, Eq. (8.76), with $\hat{h}_j$ and J_{jk} determined from step (2), which results in the next approximation for states, $|\psi_1^{(1)}(1)\rangle, \cdots, |\psi_{N_e}^{(1)}(N_e)\rangle$.
4. Repeat the procedures (2) and (3), until convergence is reached in the energy determined by Eq. (8.78).

Although the procedure of iteration within the Hartree approximation, as sketched above, is a powerful method applicable to general many-body problems, in practice, it is not applicable to actual many-electron systems because the resulting solution is not guaranteed to satisfy the symmetry requirement. Unlike the case with the helium atom that has only two electrons, it is not straightforward to check or ensure the symmetry requirement separately from the iteration procedure.

8.4.2 Hartree-Fock Approximation

The Hartree-Fock (HF) approximation is similar to the Hartree approximation except that it ensures that the symmetry property is satisfied by considering trial states that meet the symmetry condition at the outset. A well-known expression for the many-electron state as a linear combination of the products of single electron states, which satisfies the antisymmetry property, is the following Slater determinant:

$$|\Psi_{N_e}\rangle = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} |\psi_1(1)\rangle & |\psi_2(1)\rangle & \cdots & |\psi_{N_e}(1)\rangle \\ |\psi_1(2)\rangle & |\psi_2(2)\rangle & \cdots & |\psi_{N_e}(2)\rangle \\ \vdots & \vdots & \vdots & \vdots \\ |\psi_1(N_e)\rangle & |\psi_2(N_e)\rangle & \cdots & |\psi_{N_e}(N_e)\rangle \end{vmatrix}. \tag{8.79}$$

For the ground electronic state where there are $N_e = 2N_r$ electrons that completely fill in N_r orbitals, the above state can be expressed as

$$|\Psi_{2N_r}\rangle = \frac{1}{\sqrt{(2N_r)!}} \begin{vmatrix} |\phi_1(1)\rangle|\alpha(1)\rangle & |\phi_1(1)\rangle|\beta(1)\rangle & \cdots & |\phi_{N_r}(1)\rangle|\beta(1)\rangle \\ |\phi_1(2)\rangle|\alpha(2)\rangle & |\phi_1(2)\rangle|\beta(2)\rangle & \cdots & |\phi_{N_r}(2)\rangle|\beta(2)\rangle \\ \vdots & \vdots & \vdots & \vdots \\ |\phi_1(2N_r)\rangle|\alpha(2N_r)\rangle & |\phi_1(2N_r)\rangle|\beta(2N_r)\rangle & \cdots & |\phi_{N_r}(2N_r)\rangle|\beta(2N_r)\rangle \end{vmatrix} \tag{8.80}$$

Equivalently, this determinant state can also be expressed as follows:

$$|\Psi_{2N_r}\rangle = \frac{1}{\sqrt{(2N_r)!}} \sum_{\hat{P}} (-1)^{N_P} \hat{P} \left(|\phi_1(1)\rangle|\alpha(1)\rangle \cdots |\phi_{N_r}(2N_r)\rangle|\beta(2N_r)\rangle \right), \tag{8.81}$$

where $\hat{P}$ represents a permutation operation of $1, \cdots, 2N_r$ electron indices and N_P is the number of pairwise permutations constituting a given permutation.[3] It is straightforward to show that the above definition satisfies the antisymmetric property with respect to any exchange of two electron indices. Since ϕ_k's correspond to orbitals for the same atom, the following orthonormality relation holds:

$$\langle \phi_k(l)|\phi_j(l)\rangle = \delta_{kj}. \tag{8.82}$$

Now, let us consider the following Hamiltonian for $2N_r$ electrons:

$$\hat{H}_{el} = \sum_{\mu=1}^{2N_r} \hat{h}_\mu + \frac{1}{2} \sum_{\mu}^{2N_r} \sum_{\nu \neq \mu} \frac{1}{\hat{r}_{\mu\nu}}. \tag{8.83}$$

Then, the total electronic energy within the HF approximation is obtained by taking expectation value of the above Hamiltonian with respect to the antisymmetric state of $2N$ electrons, Eq. (8.81).

Expression for the Total Energy Within the HF Approximation

Taking the expectation value of the Hamiltonian $\hat{H}_{el}$ with respect to the single determinant many-electron state, Eq. (8.81), one can obtain the following expression for the HF energy:

(continued)

[3] There is well established theorem that any permutation can be expressed as composite of pairwise permutations.

$$E_{HF} = \langle \Psi_{2N_r} | \hat{H}_{el} | \Psi_{2N_r} \rangle = \sum_{\mu=1}^{2N_r} \langle \Psi_{2N_r} | \hat{h}_\mu | \Psi_{2N_r} \rangle + \frac{1}{2} \sum_{\mu}^{2N_r} \sum_{\nu \neq \mu}^{2N_r} \langle \Psi_{2N_r} | \frac{1}{\hat{r}_{\mu\nu}} | \Psi_{2N_r} \rangle$$

$$= 2 \sum_{p=1}^{N_r} I_p + \sum_{p=1}^{N_r} \sum_{q=1}^{N_r} (2J_{pq} - K_{pq}), \tag{8.84}$$

where

$$I_p = \langle \phi_p(1) | \hat{h}_1 | \phi_p(1) \rangle, \tag{8.85}$$

$$J_{pq} = \langle \phi_p(1) | \langle \phi_q(2) | \frac{1}{\hat{r}_{12}} | \phi_p(1) \rangle | \phi_q(2) \rangle, \tag{8.86}$$

$$K_{pq} = \langle \phi_p(1) | \langle \phi_q(2) | \frac{1}{\hat{r}_{12}} | \phi_q(1) \rangle | \phi_p(2) \rangle. \tag{8.87}$$

In the above expressions, I_p is the energy of the orbital p for a single electron, J_{pq} is called Coulomb integral, and K_{pq} is called exchange integral. Detailed derivation of Eq. (8.84) is provided below.

Let us consider detailed derivation of all the terms that appear in Eq. (8.84). First, the expectation value of the single electron term $\hat{h}_\mu$ is as follows:

$$\sum_{\mu=1}^{2N_r} \langle \Psi_{2N_r} | \hat{h}_\mu | \Psi_{2N_r} \rangle = \frac{1}{(2N_r)!} (2N_r - 1)! \sum_{\mu=1}^{2N_r} \sum_{p=1}^{N_r} 2 \langle \phi_p(\mu) | \hat{h}_\mu | \phi_p(\mu) \rangle$$

$$= \frac{1}{2N_r} 2 \cdot 2N_r \sum_{p=1}^{N_r} \langle \phi_p(1) | \hat{h}_1 | \phi_p(1) \rangle = 2 \sum_{p=1}^{N_r} I_p, \tag{8.88}$$

where the fact that $\langle \phi_p(\mu) | \hat{h}_\mu | \phi_p(\mu) \rangle$ is independent of the particular choice of μ has been used in replacing all $2N_r$ expressions in terms of the one with $\mu = 1$. On the other hand,

$$\sum_{\mu=1}^{2N_r} \sum_{\nu \neq \mu} \langle \Psi_{2N_r} | \frac{1}{\hat{r}_{\mu\nu}} | \Psi_{2N_r} \rangle$$

$$= \frac{1}{(2N_r)!} (2N_r - 2)! \sum_{\mu=1}^{2N_r} \sum_{\nu \neq \mu} \sum_{j=1}^{2N_r} \sum_{k \neq j} \left\{ \langle \psi_j(\mu) | \langle \psi_k(\nu) | \frac{1}{\hat{r}_{\mu\nu}} | \psi_j(\mu) \rangle | \psi_k(\nu) \rangle \right.$$

$$\left. - \langle \psi_j(\mu) | \langle \psi_k(\nu) | \frac{1}{\hat{r}_{\mu\nu}} | \psi_k(\mu) \rangle | \psi_j(\nu) \rangle \right\}$$

$$= \sum_{j=1}^{2N_r} \sum_{k \neq j} \left\{ \langle \psi_j(1) | \langle \psi_k(2) | \frac{1}{\hat{r}_{12}} | \psi_j(1) \rangle | \psi_k(2) \rangle \right.$$

$$\left. - \langle \psi_j(1) | \langle \psi_k(2) | \frac{1}{\hat{r}_{12}} | \psi_k(1) \rangle | \psi_j(2) \rangle \right\}, \tag{8.89}$$

where the negative sign for the second term within the curly bracket reflects the antisymmetric property of the Slater determinant, given by Eq. (8.81). In other words, this terms results from the component of the $1/\hat{r}_{\mu\nu}$ operator between a particular component of the $2N_r$-electron product in the bra of Eq. (8.81) and another term of the ket where two electrons μ and ν have switched their states. The resulting ket should have an opposite sign from that of the bra state because they are different by one pairwise exchange of two electrons. The second equality in Eq. (8.89) reflects the fact that the two integral terms involving μ and ν are independent of particular choice of these indices. Thus, $2N_r(2N_r-1)$ of such terms can all be replaced with the one with $\mu = 1$ and $\nu = 2$.

Note that each single electron state is a spin-orbit state. In other words, for $j = 2p-1$,

$$|\psi_{2p-1}(\mu)\rangle = |\phi_p(\mu)\rangle|\alpha(\mu)\rangle. \tag{8.90}$$

On the other hand, for $j = 2p$,

$$|\psi_{2p}(\mu)\rangle = |\phi_p(\mu)\rangle|\beta(\mu)\rangle. \tag{8.91}$$

Now, the components in the summation in Eq. (8.89) can be simplified depending on whether the indices are even or odd as follows.

For $j = 2p-1, k = 2p$ or $j = 2p, k = 2p-1$,

$$\langle \psi_j(1) | \langle \psi_k(2) | \frac{1}{\hat{r}_{12}} | \psi_j(1) \rangle | \psi_k(2) \rangle$$

$$= \langle \phi_p(1) | \phi_p(2) | \frac{1}{\hat{r}_{12}} | \phi_p(1) \rangle | \phi_p(2) \rangle = J_{pp}. \tag{8.92}$$

On the other hand, the second term that results from the exchange of two electrons in this case is zero as follows:

$$\langle \psi_j(1) | \langle \psi_k(2) | \frac{1}{\hat{r}_{12}} | \psi_k(1) \rangle | \psi_j(2) \rangle = 0. \tag{8.93}$$

This is because the spin α and β states are orthogonal to each other.

For $j = 2p-1, k = 2q-1$ or $j = 2p, k = 2q$ with $p \neq q$,

$$\langle\psi_j(1)|\langle\psi_k(2)|\frac{1}{\hat{r}_{12}}|\psi_j(1)\rangle|\psi_k(2)\rangle$$
$$= \langle\phi_p(1)|\phi_q(2)|\frac{1}{\hat{r}_{12}}|\phi_p(1)\rangle|\phi_q(2)\rangle = J_{pq}. \tag{8.94}$$

On the other hand, for this case,

$$\langle\psi_j(1)|\langle\psi_k(2)|\frac{1}{\hat{r}_{12}}|\psi_k(1)\rangle|\psi_j(2)\rangle$$
$$= \langle\phi_p(1)|\langle\phi_q(2)|\frac{1}{\hat{r}_{12}}|\phi_q(1)\rangle|\phi_p(2)\rangle = K_{pq}, \tag{8.95}$$

which is nonzero in general.

For $j = 2p-1, k = 2q$ or $j = 2p, k = 2q-1$ with $p \neq q$,

$$\langle\psi_j(1)|\langle\psi_k(2)|\frac{1}{\hat{r}_{12}}|\psi_j(1)\rangle|\psi_k(2)\rangle$$
$$= \langle\phi_p(1)|\phi_q(2)|\frac{1}{\hat{r}_{12}}|\phi_p(1)\rangle|\phi_q(2)\rangle = J_{pq}. \tag{8.96}$$

On the other hand, the second exchange term for this case is zero as follows:

$$\langle\psi_j(1)|\langle\psi_k(2)|\frac{1}{\hat{r}_{12}}|\psi_k(1)\rangle|\psi_j(2)\rangle = 0. \tag{8.97}$$

This is because the spin α and β states are orthogonal to each other.

Combining all of the above cases, Eq. (8.89) can be expressed as

$$\sum_{j=1}^{2N_r}\sum_{k\neq j}\left\{\langle\psi_j(1)|\langle\psi_k(2)|\frac{1}{\hat{r}_{12}}|\psi_j(1)\rangle|\psi_k(2)\rangle \right.$$
$$\left. -\langle\psi_j(1)|\langle\psi_k(2)|\frac{1}{\hat{r}_{12}}|\psi_k(1)\rangle|\psi_j(2)\rangle\right\}$$
$$= 2\sum_{p=1}^{N_r}\left\{J_{pp} + \sum_{q\neq p}(2J_{pq} - K_{pq})\right\}$$
$$= 2\sum_{p=1}^{N_r}\sum_{q=1}^{N_r}\left\{2J_{pq} - K_{pq}\right\}, \tag{8.98}$$

where, in the last equality, the fact that $K_{pp} = J_{pp}$ has been used. This completes the proof of Eq. (8.84).

Having demonstrated the validity of Eq. (8.84), let us now consider its relationship with the single electron picture. For this, let us consider the following effective single electron Hamiltonian operator:

$$\hat{H}_p(1) = \hat{h}_1 + \sum_{q=1}^{N_r} \left(2\hat{J}_{pq}(1) - \hat{K}_{pq}(1)\right), \tag{8.99}$$

where $\hat{J}_{pq}(1)$ and $\hat{K}_{pq}(1)$ are operators defined for electron 1 by the following relations:

$$\hat{J}_{pq}(1)|\phi_p(1)\rangle = \left(\langle\phi_q(2)|\frac{1}{\hat{r}_{12}}|\phi_q(2)\rangle\right)|\phi_p(1)\rangle, \tag{8.100}$$

$$\hat{K}_{pq}(1)|\phi_p(1)\rangle = \left(\langle\phi_q(2)|\frac{1}{\hat{r}_{12}}|\phi_p(2)\rangle\right)|\phi_q(1)\rangle. \tag{8.101}$$

Let us assume that $|\phi_p(1)\rangle$ is the eigenstate of $\hat{H}_p(1)$ with eigenvalue $\mathcal{E}_p$ as follows:

$$\hat{H}_p(1)|\phi_p(1)\rangle = \left(\hat{h}_1 + \sum_{q=1}^{N_r} \left(2\hat{J}_{pq}(1) - \hat{K}_{pq}(1)\right)\right)|\phi_p(1)\rangle = \mathcal{E}_p|\phi_p(1)\rangle. \tag{8.102}$$

Then, taking inner product of the above equation with $\langle\phi_p(1)|$, we obtain the following expression:

$$\mathcal{E}_p = I_p + \sum_{q=1}^{N_r}(2J_{pq} - K_{pq}). \tag{8.103}$$

This is the energy of each orbital. In this expression, $2J_{pq}$ is the regular Coulomb interaction term representing interactions with other electrons. The factor of 2 in this term accounts for the contributions of both spin up and down states. On the other hand, $-K_{pq}$ represents purely quantum mechanical interaction that comes from exchange of two electrons. This is nonzero only when the two electrons are in the same spin state. Note that the interaction between two electrons in the same orbital, J_{pp}, is also included in Eq. (8.103), for which $K_{pp} = J_{pp}$. With the above expression, the HF energy can be expressed as follows:

$$E_{HF} = 2\sum_{p=1}^{N_r}\mathcal{E}_p - \sum_{p=1}^{N_r}\sum_{q=1}^{N_r}(2J_{pq} - K_{pq}). \tag{8.104}$$

Equations (8.102)–(8.104) serve as the formal framework for the iteration procedure in the HF approximation. Thus, one can continue the following procedure until convergence in E_{HF} is reached.

1. Choose the initial guess states for $|\phi_1^{(0)}(1)\rangle, \cdots, |\phi_{N_r}^{(0)}(1)\rangle$, which are all orthogonal to each other.
2. Determine $\hat{h}_1$, $\hat{J}_{pq}(1)$, and $\hat{K}_{pq}(1)$ using the states determined in step (1).
3. Solve the one electron Schrödinger equation, Eq. (8.102), with $\hat{h}_1$, $\hat{J}_{pq}(1)$, and $\hat{K}_{pq}(1)$ determined from step (2), which results in the next approximation for the orbital states, $|\phi_1^{(1)}(1)\rangle, \cdots, |\phi_{N_r}^{(1)}(1)\rangle$.
4. Repeat the procedures (2) and (3), until convergence is reached in the energy determined by Eq. (8.104).

Although the above HF approximation accounts for the effect of many electrons on average, it misses the effects of correlation between different electrons, which requires going beyond the assumption of trial state as a single Slater-type determinant. The approach of assuming the state as a linear combination of multiple determinants is usually called multi-configuration methods. Another important effect that is missing in the HF approximation described above is the spin-orbit interaction and/or relativistic effect, which become important for heavy atoms.

8.5 Summary and Questions

For many-electron atoms, the corresponding time independent Schrödinger equations cannot be solved exactly. However, due to the spherical symmetry of the system having only one nuclear center and the Pauli exclusion principle that leads to substantial reduction of repulsive interactions between electrons, it is possible to come up with an approximate scheme that is simple enough to offer good physical insights into many-electron atoms. The simplest of this kind is the independent electron model that assumes that the collection of many-electron states can be viewed as filling up electrons one by one on top of others according to the Aufbau (Building-up) principle that prescribes putting electrons in single electron orbitals that are available and have the lowest possible energies.

Within the independent electron model, the degeneracy of the single electron orbitals for the same value of the principal quantum number is lifted because the effective electron-nuclear potential, even though it remains centrally symmetric, is no longer in Coulombic form. In general, orbitals with smaller orbital angular momentum quantum number l have lower energy than those with higher l for the same principal quantum number n. This is because the former tends to penetrate better into the region closer to the nucleus than the latter. While these energy differences between different values of l are small compared to the principal energy differences for small n, the two become comparable as n becomes large. This results in unique properties of transition metal elements, lanthanides, and actinides.

For many electron atoms, the sum of total orbital angular momenta of electrons and total spin of electrons remains conserved and the corresponding quantum number, normally called J, serves as a good quantum number. For the case where the spin-orbit interactions are small, which remains a good approximation except for heavy atoms, the total orbital quantum number L and the total spin S serve as nearly

good quantum number and can be effectively used to specify different electronic states. With proper consideration of the Pauli exclusion principle that forbids having two electrons in the exactly the same spin-orbit states, it is possible to come up with all distinctive states that can be specified by the values of L, S, and J. Then, relative orders of these states can be determined according to the application of Hund's rules and Lande's interval rule.

Selection rules for the atomic spectroscopy of many atoms can be understood on the basis of terms classified according to the values of L, S, and J and employing the fact that the interaction with the radiation is through the dipole operator, which causes the change of L at most one and leaves S to remain unchanged. The fact that the dipole operator has odd inversion symmetry also leads to Laporte's rule for allowed transitions.

More quantitative description of many-electron states can be conducted by applying the variational principle in a self-consistent way. The simplest of this is called the Hartree approximation, which however does not take the symmetry property of many electron states into consideration. A proper approach that also accounts for the Pauli-exclusion principle is the HF approximation. This serves as fairly accurate method of calculating many electron states although it does not account for correlation effects of many electrons and other effects that require more advanced theories.

Questions

- What is the physical basis for Aufbau principle? Can this be justified based on the perturbation theory?
- What is the difference between a configuration and a state for many electron systems?
- What is the major difference between LS-coupling and jj-coupling schemes?
- Why are not all combinations of L and S possible for states for electrons occupying the same orbital?
- How can Hund's rules be understood? Can they be violated?
- What is the physical origin of Lande's interval rule?
- What are selection rules for L, S, and J in electronic absorption or emission involving electronic states of many electron atoms? How can they be explained?
- Can one apply the Hartree approximation for a collection of identical bosons?
- What is the origin of the exchange interaction in the HF approximation?

Exercise Problems with Solutions

8.1 Find out all the atomic term symbols for p^5d^1, and list them in the order of increasing energy (assuming Lande's interval rule for more than half filled orbitals.).

Solution 8.1 p^5d^1 has the same terms as p^1d^1. Thus, we consider the latter. Since there are two electrons with $l_1 = 1$ and $l_2 = 2$ occupying different orbitals, $L = 1$, 2, and 3, and for each case $S = 0$ and 1 are possible. Therefore, the following combinations and terms are possible.

L	S	J	Terms
1	0	1	${}^1\mathrm{P}_1$
1	1	0,1,2	${}^3\mathrm{P}_0$, ${}^3\mathrm{P}_1$, ${}^3\mathrm{P}_2$
2	0	2	${}^1\mathrm{D}_2$
2	1	1,2, 3	${}^3\mathrm{D}_1$, ${}^3\mathrm{D}_2$, ${}^3\mathrm{D}_3$
3	0	3	${}^1\mathrm{F}_3$
3	1	2, 3, 4	${}^3\mathrm{F}_2$, ${}^3\mathrm{F}_3$, ${}^3\mathrm{F}_4$

The order of the above terms from the lowest to the highest energies is as follows:

$$ {}^3\mathrm{F}_4,\ {}^3\mathrm{F}_3,\ {}^3\mathrm{F}_2,\ {}^3\mathrm{D}_3,\ {}^3\mathrm{D}_2,\ {}^3\mathrm{D}_1,\ {}^3\mathrm{P}_2,\ {}^3\mathrm{P}_1,\ {}^3\mathrm{P}_0,\ {}^1\mathrm{F}_3,\ {}^1\mathrm{D}_2,\ {}^1\mathrm{P}_1 $$

8.2 Find all the atomic term symbols for d^2 configuration, and list them in the order of increasing energy. Specify where Hund's rule and Lande's interval rule are used.

Solution 8.2 For the given configuration, there are the following ten states of (l_z, s_z) for one electron:

$$ a : (2, \tfrac{1}{2}) \qquad b : (1, \tfrac{1}{2}) \qquad c : (0, \tfrac{1}{2}) \qquad d : (-1, \tfrac{1}{2}) \qquad e : (-2, \tfrac{1}{2}) $$

$$ a' : (2, \tfrac{1}{2}) \qquad b' : (1, \tfrac{1}{2}) \qquad c' : (0, \tfrac{1}{2}) \qquad d' : (-1, \tfrac{1}{2}) \qquad e' : (-2, \tfrac{1}{2}) $$

The combination of two different states among the above leads to the following pairs for (L_z, S_z):

$$
\begin{array}{lllll}
a+a' : (4,0) & a+b : (3,1) & a+c : (2,1) & a+d : (1,1) & a+e : (0,1) \\
 & a+b' : (3,0) & a+c' : (2,0) & b+c : (1,1) & b+d : (0,1) \\
 & a'+b : (3,0) & a'+c : (2,0) & a+d' : (1,0) & a+e' : (0,0) \\
 & & b+b' : (2,0) & a'+d : (1,0) & a'+e : (0,0) \\
 & & & b+c' : (1,0) & b+d' : (0,0) \\
 & & & b'+c : (1,0) & b'+d : (0,0) \\
 & & & & c+c' : (0,0)
\end{array}
$$

In the above list, the presence of $(4, 0)$ means that the combination of $L = 4$ and $S = 0$ exists, for which $(3, 0)$, $(2, 0)$, $(1, 0)$, and $(0, 0)$ can also be removed from the list. The remaining list thus becomes

$$
\begin{array}{cccc}
(3, 1) & (2, 1) & (1, 1) & (0, 1) \\
(3, 0) & (2, 0) & (1, 1) & (0, 1) \\
 & (2, 0) & (1, 0) & (0, 0) \\
 & & (1, 0) & (0, 0) \\
 & & (1, 0) & (0, 0) \\
 & & & (0, 0)
\end{array}
$$

where we have removed the combinations of labels how the above pairs are formed because they are not important for determining the terms. In the above list, the presence of (3, 1) means that the combination of $L = 3$ and $S = 1$ exists, for which (3, 0), (2, 1), (2, 0), (1, 1), (1, 0), (0, 1), (0, 0) can also be removed from the list. The remaining list thus becomes

$$
\begin{array}{ccc}
(2, 0) & (1, 1) & (0, 1) \\
 & (1, 0) & (0, 0) \\
 & (1, 0) & (0, 0) \\
 & & (0, 0)
\end{array}
$$

In the above list, the presence of (2, 0) means that the combination of $L = 2$ and $S = 0$ exists, for which (1, 0) and (0, 0) can also be removed from the list. The remaining list thus becomes

$$
\begin{array}{cc}
(1, 1) & (0, 1) \\
(1, 0) & (0, 0) \\
 & (0, 0)
\end{array}
$$

In the above list, the presence of (1, 1) means that the combination of $L = 1$ and $S = 1$ exists, for which (1, 0), (0, 1), and (0, 0) can also be removed from the list. As a result, the only remaining list becomes (0, 0), which corresponds to $L = 0$ and $S = 0$. Summing up all of those identified above, we find that

L	S	J	Terms
4	0	4	$^1G_4$
3	1	2, 3, 4	$^3F_2$, $^3F_3$, $^3F_4$
2	0	2	$^1D_2$
2	1	0, 1, 2	$^3P_0$, $^3P_1$, $^3P_2$
0	0	0	$^1S_0$

Applying Hund's rules and Lande's rule, terms from the lowest energy to the highest energy can be ordered as follows:

$$^3F_2,\ ^3F_3,\ ^3F_4,\ ^3P_0,\ ^3P_1,\ ^3P_2,\ ^1G_4,\ ^1D_2,\ ^1S_0$$

8.3 For an oxygen atom in the ground configuration [He]$2s^2 2p^4$, find out the term symbol for the ground electronic state. Assuming that the oxygen atom makes transition to an excited state configuration [He]$2s^2 2p^3 3d^1$, find out term symbols for all the excited states to which the transition from the ground electronic state is allowed.

Solution 8.3 $2s^2p^4$ has the same terms as p^2, for which, as explained in the main text, the following terms can be identified:

$$^1D_2,\ ^3P_2,\ ^3P_1,\ ^3P_0,\ ^1S_0$$

Since the p orbital is more than half-filled, according to Lande's interval rule, $^3P_2$ is the ground state term. Now let us consider possible terms for the excited configuration, which is equivalent to $2p^3 3d^1$. As described in the main text, for p^3, the following three cases are possible.

$$L = 2,\ S = \frac{1}{2}$$
$$L = 1,\ S = \frac{1}{2}$$
$$L = 0,\ S = \frac{3}{2}$$

For each case, adding $l = 2$ and $s = 1/2$ of the d orbital electron, we obtain the following combinations:

$$L = 0,\ 1,\ 2,\ 3,\ 4;\ S = 0,\ 1$$
$$L = 1,\ 2,\ 3;\ S = 0,\ 1$$
$$L = 2,;\ S = 1,\ 2$$

Therefore, possible terms can be obtained as follows:

L	S	J	Terms
0	0	0	$^1S_0$
0	1	1	$^3S_1$
1	0	1	$^1P_1$
1	1	0,1,2	$^3P_0, {}^3P_1, {}^3P_2$
2	0	2	$^1D_2$
2	1	1, 2, 3	$^3D_1, {}^3D_2, {}^3D_3$
2	2	0, 1, 2, 3, 4	$^5D_0, {}^5D_1, {}^5D_2, {}^5D_3, {}^5D_4$
3	0	3	$^1F_3$
3	1	2, 3, 4	$^3F_2, {}^3F_3, {}^3F_4$
4	0	4	$^1G_4$
4	1	3, 4, 5	$^3G_3, {}^3G_4, {}^3G_5$

Among the terms above, transition from $^3P_2$ to the following terms are allowed: $^3S_1$, $^3P_1$, $^3P_2$, $^3D_1$, $^3D_2$, $^3D_3$

Problems

8.4 Find out all the atomic term symbols for $s^1p^5d^1$, and list them in the order of increasing energy (assuming Lande's interval rule for more than half filled orbitals.).

8.5 For an excited configuration of C given by $1s^22s^12p^3$, find out all possible terms.

8.6 For the ground electronic state of Be with the configuration $1s^22s^2$, find out total electronic energy within the Hartree-Fock approximation by employing Eq. (8.84). Express your answer in terms of the following quantities:

$$I_{1s} = \langle 1s(1)|\hat{h}_1|1s(1)\rangle,$$

$$I_{2s} = \langle 2s(1)|\hat{h}_1|2s(1)\rangle,$$

$$J_{1s1s} = \langle 1s(1)|\langle 1s(2)|\frac{1}{\hat{r}_{12}}|1s(2)\rangle|1s(1)\rangle,$$

$$J_{2s2s} = \langle 2s(1)|\langle 2s(2)|\frac{1}{\hat{r}_{12}}|2s(2)\rangle|2s(1)\rangle,$$

$$J_{1s2s} = \langle 1s(1)|\langle 2s(2)|\frac{1}{\hat{r}_{12}}|2s(2)\rangle|1s(1)\rangle,$$

$$K_{1s2s} = \langle 1s(1)|\langle 2s(2)|\frac{1}{\hat{r}_{12}}|2s(1)\rangle|1s(2)\rangle.$$

Chapter 9
Polyatomic Molecules and Molecular Spectroscopy



We have sought for firm ground and found none. The deeper we penetrate, the more restless becomes the universe; all is rushing about and vibrating in a wild dance.

– Max Born

Abstract This chapter provides a general quantum mechanical account of polyatomic molecules, and describes the Born-Oppenheimer approximation that allows calculation of adiabatic electronic states for fixed nuclear coordinates. Taking diatomic molecules as examples, independent electron model and the approximation of linear combination of atomic orbitals as molecular orbitals (LCAO-MO) are described, and the molecular term symbols for corresponding electronic states are explained. As the next example, the LCAO-MO approximation with additional assumptions due to Hückel is used to describe electronic states of π-conjugated molecules. The chapter then provides a brief overview of the group theory and its applications for constructing MOs and analyses of vibrational spectroscopy.

The Hamiltonian operator for a polyatomic molecule with N_u nuclei and N_e electrons consists of two terms as follows:

$$\hat{H}_M = \hat{H}_{nu} + \hat{H}_{en}, \tag{9.1}$$

where $\hat{H}_{nu}$ represents the nuclear kinetic and potential energies, and $\hat{H}_{en}$ represents the kinetic and potential energies of electrons. The potential energy of electrons includes both electron-nuclei interactions and those between electrons. In atomic

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units, these two terms are expressed as

$$\hat{H}_{nu} = \sum_{c=1}^{N_u} \frac{\hat{\mathbf{P}}_c^2}{2M_c} + \frac{1}{2} \sum_{c=1}^{N_u} \sum_{c' \neq c} \frac{Z_c Z_{c'}}{|\mathbf{R}_c - \mathbf{R}_{c'}|}, \tag{9.2}$$

$$\hat{H}_{en} = \sum_{\mu=1}^{N_e} \frac{\hat{\mathbf{p}}_\mu^2}{2} - \sum_{\mu=1}^{N_e} \sum_{c=1}^{N_u} \frac{Z_c e^2}{|\hat{\mathbf{r}}_\mu - \hat{\mathbf{R}}_c|} + \frac{1}{2} \sum_{\mu=1}^{N_e} \sum_{\nu \neq \mu} \frac{1}{|\hat{\mathbf{r}}_\mu - \hat{\mathbf{r}}_\nu|}. \tag{9.3}$$

In Eq. (9.2), M_c, $\hat{\mathbf{P}}_c$, $\hat{\mathbf{R}}_c$, and Z_c are the mass, momentum operator, position operator, and charge of the nucleus labeled as c. In Eq. (9.3), $\hat{\mathbf{p}}_\mu$ and $\hat{\mathbf{r}}_\mu$ are the momentum and position operators of the electron labeled as μ.

Let us denote the eigenstate of the above molecular Hamiltonian $\hat{H}_M$ as $|\Psi_M\rangle$, for which the time independent Schrödinger equation is

$$\hat{H}_M |\Psi_M\rangle = (\hat{H}_{nu} + \hat{H}_{en}) |\Psi_M\rangle = E_M |\Psi_M\rangle. \tag{9.4}$$

Solving the above equation is challenging even numerically. In particular, the large disparity of the masses of electrons and nuclei make it difficult to come up with common length and energy scales applicable to both of them. Thus, due to both conceptual and numerical reasons, it is much more beneficial to treat them at different levels. The standard approach for this is the Born-Oppenheimer (BO) approximation that treats nuclear motions adiabatically and ignores the coupling between electron and nuclear kinetic energies as described in detail below.

9.1 Born-Oppenheimer Approximation

Let us denote the whole set of nuclear coordinates as $\mathbf{R} = (\mathbf{R}_1, \cdots, \mathbf{R}_{N_u})$ and the corresponding position state bra of the nuclear coordinates as $\langle \mathbf{R}|$. Taking inner product of this with Eq. (9.4), we obtain

$$\langle \mathbf{R}|\hat{H}_M|\Psi_M\rangle = \langle \mathbf{R}|\hat{H}_{nu}|\Psi_M\rangle + \langle \mathbf{R}|\hat{H}_{en}|\Psi_M\rangle = E_M \langle \mathbf{R}|\Psi_M\rangle. \tag{9.5}$$

In the above expression, the nuclear term involving $\hat{H}_{nu}$ can be calculated using Eq. (9.2) and is expressed as

$$\langle \mathbf{R}|\hat{H}_{nu}|\Psi_M\rangle = \left\{ -\sum_{c=1}^{N_u} \frac{\hbar^2}{2M_c} \nabla_c^2 + \frac{1}{2} \sum_{c=1}^{N_u} \sum_{c' \neq c} \frac{Z_c Z_{c'}}{|\mathbf{R}_c - \mathbf{R}_{c'}|} \right\} \langle \mathbf{R}|\Psi_M\rangle. \tag{9.6}$$

On the other hand, the term involving $\hat{H}_{en}$ in Eq. (9.5) can be simply expressed as

$$\langle \mathbf{R}|\hat{H}_{en}|\Psi_M\rangle = \hat{H}_{en}(\mathbf{R})\langle \mathbf{R}|\Psi_M\rangle, \tag{9.7}$$

where $\hat{H}_{en}(\mathbf{R})$ is the same as Eq. (9.3) except that $\hat{\mathbf{R}}$ is replaced with $\mathbf{R}$ as follows:

$$\hat{H}_{en}(\mathbf{R}) = \sum_{\mu=1}^{N_e} \frac{\hat{\mathbf{p}}_\mu^2}{2} - \sum_{\mu=1}^{N_e}\sum_{c=1}^{N_u} \frac{Z_c e^2}{|\hat{\mathbf{r}}_\mu - \mathbf{R}_c|} + \frac{1}{2}\sum_{\mu=1}^{N_e}\sum_{\nu\neq\mu} \frac{1}{|\hat{\mathbf{r}}_\mu - \hat{\mathbf{r}}_\nu|}. \tag{9.8}$$

Equation (9.8) represents the Hamiltonian for electrons with fixed nuclear coordinates as parameters. Let us now define adiabatic electronic states as eigenstates of this Hamiltonian. Thus,

$$\hat{H}_{en}(\mathbf{R})|\psi_{e,a}(\mathbf{R})\rangle = E_{e,a}(\mathbf{R})|\psi_{e,a}(\mathbf{R})\rangle, \tag{9.9}$$

where a denotes the index specifying different adiabatic electronic eigenstates for the fixed nuclei.

Before moving to the next step, it is worthwhile to note the parametric dependence of Eq. (9.9) on the nuclear coordinates $\mathbf{R} = (\mathbf{R}_1, \cdots, \mathbf{R}_{N_u})$. As indicated, both the eigenstates and eigenvalues depend parametrically on $\mathbf{R}$. Although not shown, in fact, even the index a depends implicitly on $\mathbf{R}$. As a consequence, two different adiabatic states for two different nuclear coordinates are not in general orthogonal as indicated below.

$$\langle \psi_{e,a'}(\mathbf{R}')|\psi_{e,a}(\mathbf{R})\rangle \neq 0. \tag{9.10}$$

Once we have specified an adiabatic electronic state $|\psi_{e,a}(\mathbf{R})\rangle$, let us assume that the inner product of $\langle \mathbf{R}|$ with the total molecular wavefunction $|\Psi_M\rangle$ can be expressed as[1]

$$\langle \mathbf{R}|\Psi_M\rangle = \psi_{nu,a}(\mathbf{R})|\psi_{e,a}(\mathbf{R})\rangle. \tag{9.11}$$

The implication of the above expression is that the molecular state at $\mathbf{R}$ is defined by electrons in the particular adiabatic state $|\psi_{e,a}(\mathbf{R})\rangle$, whereas the wavefunction for nuclei is $\psi_{nu,a}(\mathbf{R})$. Employing Eq. (9.11) in Eq. (9.7), we obtain

$$\hat{H}_{en}(\mathbf{R})\langle \mathbf{R}|\Psi_M\rangle = \hat{H}_{en}(\mathbf{R})\psi_{nu,a}(\mathbf{R})|\psi_{e,a}(\mathbf{R})\rangle = \psi_{nu,a}(\mathbf{R})\hat{H}_{en}(\mathbf{R})|\psi_{e,a}(\mathbf{R})\rangle, \tag{9.12}$$

where the second equality results from the fact that $\hat{H}_{en}(\mathbf{R})$ does not involve any derivative with respect to nuclear coordinates. On the other hand, employing

[1] More generally, one can consider a linear combination of these.

Eq. (9.11) in Eq. (9.6), we obtain

$$\langle \mathbf{R}|\hat{H}_{nu}|\Psi_M\rangle = \left\{ -\sum_{c=1}^{N_u} \frac{\hbar^2}{2M_c}\nabla_c^2 + \frac{1}{2}\sum_{c=1}^{N_u}\sum_{c'\neq c} \frac{Z_c Z_{c'}}{|\mathbf{R}_c - \mathbf{R}_{c'}|} \right\} \psi_{nu,a}(\mathbf{R})|\psi_{e,a}(\mathbf{R})\rangle. \tag{9.13}$$

In the above equation, due to the dependence of the electronic state $|\psi_{e,a}(\mathbf{R})\rangle$ on the nuclear coordinates, derivatives with respect to nuclear coordinates entail couplings between electronic and nuclear degrees of freedom as follows:

$$\begin{aligned}\nabla_c^2(\psi_{nu,a}(\mathbf{R})|\psi_{e,a}(\mathbf{R})\rangle) = |\psi_{e,a}(\mathbf{R})\rangle\nabla_c^2\psi_{nu,a}(\mathbf{R}) + 2\left(\nabla_c|\psi_{e,a}(\mathbf{R})\rangle\right)\cdot\left(\nabla_c\psi_{nu,a}(\mathbf{R})\right) \\ + \left(\nabla_c^2|\psi_{e,a}(\mathbf{R})\rangle\right)\psi_{nu,a}(\mathbf{R}).\end{aligned} \tag{9.14}$$

In principle, the molecular Schrödinger equation, Eq. (9.5), can be solved by employing Eq. (9.13) including all the derivative coupling terms as indicated above. However, this is computationally challenging, and is not necessary typically because the first and second terms in the righthand side of the above equation are very small compared to the first term. The BO approximation is to ignore these small terms[2] and to employ the following simplification:

$$\nabla_c^2(\psi_{nu,a}(\mathbf{R})|\psi_{e,a}(\mathbf{R})\rangle) \approx |\psi_{e,a}(\mathbf{R})\rangle\nabla_c^2\psi_{nu,a}(\mathbf{R}). \tag{9.15}$$

Within the BO approximation as noted above, using Eq. (9.11) in Eq. (9.5) now leads to

$$\begin{aligned}&|\psi_{e,a}(\mathbf{R})\rangle\left\{ -\sum_{c=1}^{N_u} \frac{\hbar^2}{2M_c}\nabla_c^2 + \frac{1}{2}\sum_{c=1}^{N_u}\sum_{c'\neq c} \frac{Z_c Z_{c'}}{|\mathbf{R}_c - \mathbf{R}_{c'}|} + E_{e,a}(\mathbf{R}) \right\} \psi_{n,a}(\mathbf{R}) \\ &= E_M|\psi_{e,a}(\mathbf{R})\rangle\psi_{nu,a}(\mathbf{R}).\end{aligned} \tag{9.16}$$

The above equation implies that the electronic Schrödinger equation, Eq. (9.11), can be solved for all values (practically only for important region) of $\mathbf{R}$, from which the electronic energy $E_{e,a}(\mathbf{R})$ for each of the eigenstate can be determined. Combination of this with the nuclear potential energy leads to the following full BO

[2] In case two or more adiabatic electronic states are degenerate or close to each other for certain value of $\mathbf{R}$, these terms cannot be ignored and result in nonadiabatic effects. Nonadiabatic effects can be significant for bond forming or breaking situations, excited electronic states, and processes involving proton or electron transfer.

potential energy for the nuclear degrees of freedom:

$$V_{BO,a}(\mathbf{R}) = \frac{1}{2}\sum_{c=1}^{N_u}\sum_{c'\neq c}^{N_u}\frac{Z_c Z_{c'}}{|\mathbf{R}_c - \mathbf{R}_{c'}|} + E_{e,a}(\mathbf{R}). \tag{9.17}$$

Taking inner product of Eq. (9.16) with $\langle\psi_e(\mathbf{R})|$ and employing the above definition of $V_{BO,a}(\mathbf{R})$, we thus obtain the following nuclear Schrödinger equation (in Schrödinger's formulation):

$$\left\{-\sum_{c=1}^{N_u}\frac{\hbar^2}{2M_c}\nabla_c^2 + V_{BO,a}(\mathbf{R})\right\}\psi_{nu,a}(\mathbf{R}) = E_M\psi_{nu,a}(\mathbf{R}). \tag{9.18}$$

Alternatively, introducing the nuclear state $|\psi_{nu,a}\rangle$ such that $\psi_{nu,a}(\mathbf{R}) = \langle\mathbf{R}|\psi_{nu,a}\rangle$, the above Schrödinger equation can be expressed in the Dirac notation as follows:

$$\left\{\sum_{c=1}^{N_u}\frac{\hat{\mathbf{P}}_c^2}{2M_c} + V_{BO,a}(\hat{\mathbf{R}})\right\}|\psi_{nu,a}\rangle = E_M|\psi_{nu,a}\rangle. \tag{9.19}$$

Solution of the above equation completes the calculation of the molecular eigenstate within the BO approximation and the total molecular energy E_M.

9.2 Molecular Orbitals and Electronic Configurations for Diatomic Molecules

This section provides more detailed consideration of diatomic molecules, as the simplest examples of polyatomic molecules. The electronic Hamiltonian and Schrödinger equation based on the BO approximation are presented in detail. A simple molecular orbital theory for approximating these electronic states [1] is summarized, which offers clear understanding of important qualitative features observed for these systems.

9.2.1 Example of H_2

For H_2 molecule, the nuclear and electronic components of the molecular Hamiltonian constituting Eq. (9.1) are

$$\hat{H}_{nu} = \frac{\hat{\mathbf{P}}_A^2}{2M} + \frac{\hat{\mathbf{P}}_B^2}{2M} + \frac{1}{|\hat{\mathbf{R}}_A - \hat{\mathbf{R}}_B|}, \tag{9.20}$$

$$\hat{H}_{en} = \frac{\hat{\mathbf{p}}_1^2}{2} + \frac{\hat{\mathbf{p}}_2^2}{2} - \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{R}}_A|} - \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{R}}_B|} - \frac{1}{|\hat{\mathbf{r}}_2 - \hat{\mathbf{R}}_A|} - \frac{1}{|\hat{\mathbf{r}}_2 - \hat{\mathbf{R}}_B|} + \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|}. \tag{9.21}$$

Thus, the electronic Hamiltonian for fixed values of $\mathbf{R}_A$ and $\mathbf{R}_B$, defined by Eq. (9.3), for the present case is

$$\begin{aligned} \hat{H}_{en}(\mathbf{R}_A, \mathbf{R}_B) &= \frac{\hat{\mathbf{p}}_1^2}{2} + \frac{\hat{\mathbf{p}}_2^2}{2} - \frac{1}{|\hat{\mathbf{r}}_1 - \mathbf{R}_A|} - \frac{1}{|\hat{\mathbf{r}}_1 - \mathbf{R}_B|} \\ &\quad - \frac{1}{|\hat{\mathbf{r}}_2 - \mathbf{R}_A|} - \frac{1}{|\hat{\mathbf{r}}_2 - \mathbf{R}_B|} + \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|} \\ &= \frac{\hat{\mathbf{p}}_1^2}{2} + \frac{\hat{\mathbf{p}}_2^2}{2} - \frac{1}{\hat{r}_{1A}} - \frac{1}{\hat{r}_{1B}} - \frac{1}{\hat{r}_{2A}} - \frac{1}{\hat{r}_{2B}} + \frac{1}{\hat{r}_{12}}. \end{aligned} \tag{9.22}$$

Although the above Hamiltonian corresponds to the simplest electronic Hamiltonian of all polyatomic molecules, it is not amenable for an analytic solution. Thus, approximations are needed. As in the case of many-electron atoms, where the solution for hydrogen atom serves as a good basis for constructing states for many electrons, one can use the electronic states for H_2^+, for which exact analytic or reasonably good approximations exists, as a useful basis for constructing states for two or many electrons. The simplest approximation of this nature is called the linear combination of atomic orbitals as molecular orbital (LCAO-MO).

Within the LCAO-MO approximation, MOs are approximated as linear combinations of atomic orbitals. For example, for the ground electronic state of H_2^+, where there is a single electron, one can assume the following form for the MO:

$$|\Psi\rangle = C_A|1S_A\rangle + C_B|1S_B\rangle, \tag{9.23}$$

where $1S_A$ and $1S_A$ respectively represent the $1s$ orbital for a hydrogen atom centered at $\mathbf{R}_A$ and $\mathbf{R}_B$. Employing the variational principle, as described in Chap. 7, we can obtain the following matrix equation for C_A and C_B:

$$\begin{pmatrix} H_{AA} - E & H_{AB} - ES \\ H_{BA} - ES & H_{BB} - E \end{pmatrix} \begin{pmatrix} C_A \\ C_B \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}, \tag{9.24}$$

where

$$H_{AA}(R) = \langle 1S_A|\hat{H}_{en}(R)|1S_A\rangle, \tag{9.25}$$

$$H_{BB}(R) = \langle 1S_B|\hat{H}_{en}(R)|1S_B\rangle, \tag{9.26}$$

$$H_{AB}(R) = \langle 1S_A|\hat{H}_{en}(R)|1S_B\rangle = H_{BA}(R), \tag{9.27}$$

$$S(R) = \langle 1S_A|1S_B\rangle = \langle 1S_B|1S_A\rangle. \tag{9.28}$$

Employing the expression for the $1s$ orbital explicitly in the above expressions, it is possible to confirm the following relationship:

$$H_{AA}(R) = H_{BB}(R) = -\frac{1}{2} + J(R), \tag{9.29}$$

where

$$J(R) = e^{-2R}\left(1 + \frac{1}{R}\right) - \frac{1}{R}. \tag{9.30}$$

Similarly,

$$S(R) = e^{-R}\left(1 + R + \frac{R^2}{3}\right), \tag{9.31}$$

$$H_{AB}(R) = -\frac{S(R)}{2} + K(R), \tag{9.32}$$

where[3] $K(R) = -e^{-R}(1 + R)$.

The matrix equation, Eq. (9.24), implies that

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES \\ H_{BA} - ES & H_{BB} - E \end{vmatrix} = 0, \tag{9.33}$$

which has the following solutions:

$$E = \frac{H_{AA} \mp H_{AB}}{1 \mp S}. \tag{9.34}$$

Note that

$$H_{AA} - H_{BB} = -\frac{1}{2} + J(R) + \frac{1}{2}S(R) - K(R), \tag{9.35}$$

$$H_{AA} + H_{AB} = -\frac{1}{2} + J(R) - \frac{1}{2}S(R) + K(R). \tag{9.36}$$

[3] Note that $K(R)$ is not the exchange interaction term introduced in Chap. 8 although similar notation is used.

Therefore,

$$E_{-}(R) = \frac{-\frac{1}{2}(1 - S(R)) + J(R) - K(R)}{1 - S(R)}$$
$$= -\frac{1}{2} + \frac{J(R)}{1 - S(R)} - \frac{K(R)}{1 - S(R)}. \tag{9.37}$$

Similarly,

$$E_{+}(R) = -\frac{1}{2} + \frac{J(R)}{1 + S(R)} + \frac{K(R)}{1 + S(R)}. \tag{9.38}$$

In the above expressions, $J(R)$ represents the Coulomb interaction between the electron in orbital $1S_A$ (or $1S_B$) and the nucleus B (or A).

From Eq. (9.30), it is clear that $J(R) + 1/R > 0$ always. On the other hand, $K(R)$ represents stabilization energy due to sharing of an electron between two orbitals and is always negative. Therefore, $E_{+}(R) < E_{-}(R)$ for all values of R.

For $E_{+}(R)$, Eq. (9.24) reduces to

$$\begin{pmatrix} SH_{AA} - H_{AB} & H_{AB} - SH_{AA} \\ H_{BA} - SH_{AA} & SH_{AA} - H_{AB} \end{pmatrix} \begin{pmatrix} C_A \\ C_B \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \tag{9.39}$$

The solution for C_A and C_B satisfying the above equation is that $C_A = C_B$. Therefore, the corresponding state is $|\psi_{+}\rangle = C_A(|1S_A\rangle + |1S_B\rangle)$. The remaining coefficient C_A can be determined by the normalization condition, $\langle\psi_{+}|\psi_{+}\rangle = C_A^2(2 + 2S) = 1$. Thus, the state is given by

$$|\psi_{+}\rangle = \frac{1}{\sqrt{2(1 + S)}} \left(|1S_A\rangle + |1S_B\rangle\right). \tag{9.40}$$

For $E_{-}(R)$, Eq. (9.24) reduces to

$$\begin{pmatrix} -SH_{AA} + H_{AB} & H_{AB} - SH_{AA} \\ H_{BA} - SH_{AA} & -SH_{AA} + H_{AB} \end{pmatrix} \begin{pmatrix} C_A \\ C_B \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \tag{9.41}$$

The solution for C_A and C_B satisfying the above equation is that $C_A + C_B = 0$. Therefore, the corresponding state is $|\psi_{-}\rangle = C_A(|1S_A\rangle - |1S_B\rangle)$. The remaining coefficient C_A can also be determined by the normalization condition, $\langle\psi_{-}|\psi_{-}\rangle = C_A^2(2 - 2S) = 1$. Thus, the state is given by

$$|\psi_{-}\rangle = \frac{1}{\sqrt{2(1 - S)}} \left(|1S_A\rangle - |1S_B\rangle\right). \tag{9.42}$$

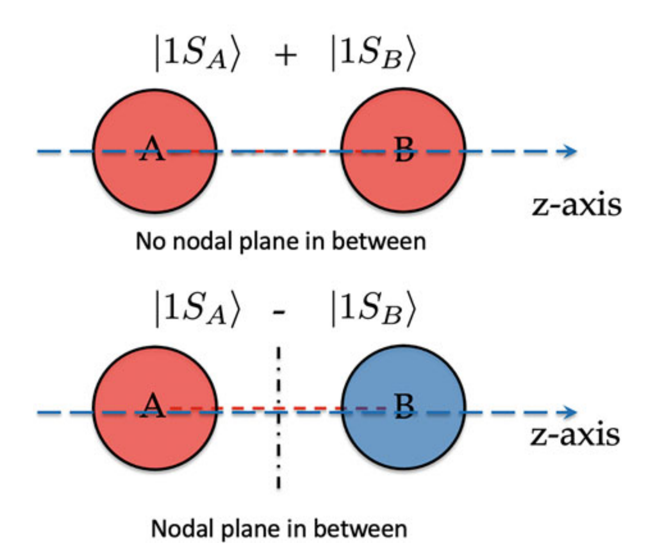


Fig. 9.1 Two LCAO-MO states formed by 1S orbitals in H_2^+

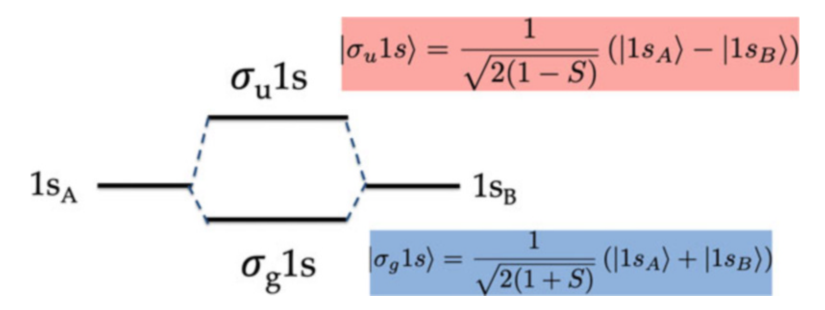


Fig. 9.2 Energy diagrams of two LCAO-MO states formed by 1S orbitals

Figure 9.1 illustrates the two orbitals $|\psi_+\rangle$ and $|\psi_-\rangle$. Because both of these states are cylindrically symmetric around the internuclear axis, they are called σ orbitals. Note that $|\psi_+\rangle$ does not have any nodal plane in between A and B and is thus symmetric with respect to inversion, whereas $|\psi_-\rangle$ has a nodal plane and is antisymmetric. Therefore, the former is denoted as[4] $|\sigma_g 1s\rangle$ while the latter as[5] $|\sigma_u 1s\rangle$.

Figure 9.2 shows the energy diagram of $|\sigma_g 1s\rangle$ and $|\sigma_u 1s\rangle$ states. As is alluded from the figure, the lowering of $E_g = E_+(R)$ from that of the atomic state is less than the relative increase of $E_u = E_-(R)$. This can in fact be proved directly.

[4] Subscript g represents gerade (even in German).

[5] Subscript u represents ungerade (odd in German).

Equations (9.37) and (9.38) can be re-expressed as

$$E_u = -\frac{1}{2} + \frac{J(R) - K(R)}{1 - S(R)} + \frac{1}{R}, \tag{9.43}$$

$$E_g = -\frac{1}{2} + \frac{J(R) + K(R)}{1 + S(R)} + \frac{1}{R}, \tag{9.44}$$

where note that $E_{1s} = -1/2$. Therefore,

$$\begin{aligned}(E_u - E_{1s}) - (E_{1s} - E_g) &= -\left(\frac{1}{1 - S(R)} - \frac{1}{1 + S(R)}\right) K(R) \\ &\quad + \left(\frac{1}{1 - S(R)} + \frac{1}{1 + S(R)}\right) J(R) + \frac{2}{R} \\ &\geq 2\left(J(R) + \frac{1}{R}\right) \geq 0. \end{aligned} \tag{9.45}$$

Thus, the amount of destabilization of energy in anti-bonding orbital is more than the amount of stabilization in bonding orbital.

9.2.2 *Molecular Orbitals and Electronic Configurations of Diatomic Molecules*

LCAO-MOs can be constructed for all other diatomic molecules in a manner similar to those for H_2 described in the previous subsection. Within the independent electron model, one can then construct the *electronic configuration* by filling electrons in available MOs, up to two electrons per each orbital so as not to violate the Pauli exclusion principle. An important quantity indicating the stability of each electronic configuration is its bond order defined below.

Bond Order (B.O.)

Given the electronic configuration, the bond order (B.O.) can be calculated as defined below.

$$\text{Bond Order (B.O.)} = \frac{1}{2}\{(\text{\# of electrons in bonding orbitals}) - (\text{\# of electrons in anti-bonding orbitals})\}$$

Let us consider the examples of diatomic molecules in the first row. For the case of H_2, the electronic configuration is $(\sigma_g 1s)^2$ and the B.O. is 1. On the other hand, for He_2, the electronic configuration is $(\sigma_g 1s)^2(\sigma_u 1s)^2$ and the B.O. is 0. Because of Eq. (9.45), the total energy of electrons for He_2 is higher than the sum of He, even within the approximation of independent electrons. Therefore, He_2 is energetically unfavorable and is not formed.

For the specification of electronic configurations of diatomic molecules with more electrons than He_2, it is necessary to consider additional MOs formed by other types of atomic orbitals. For $2s$ atomic orbitals, the MOs that can be formed are similar to those from $1s$ orbitals, and are denoted as $\sigma_g 2s$ and $\sigma_u 2s$.

The MOs formed by the three $2p$ orbitals can be classified into two different groups. The $2p_z$ orbitals form σ orbitals as follows:

$$|\sigma_g 2p_z\rangle \propto (|2p_{z,A}\rangle - |2p_{z,B}\rangle), \tag{9.46}$$

$$|\sigma_u 2p_z\rangle \propto (|2p_{z,A}\rangle + |2p_{z,B}\rangle). \tag{9.47}$$

Note that the bonding orbital in this case is formed by the difference (instead of the sum) of the two $2p_z$ atomic orbitals. This way, the two has the same phase in the region between the two nuclei. Bonding and anti-bonding orbitals that can be formed by the two atomic orbitals are illustrated in Fig. 9.3.

On the other hand, p_x and p_y orbitals form π MOs as follows:

$$|\pi_u 2p_y\rangle \propto (|2p_{y,A}\rangle + |2p_{y,B}\rangle), \tag{9.48}$$

$$|\pi_u 2p_x\rangle \propto (|2p_{x,A}\rangle + |2p_{x,B}\rangle), \tag{9.49}$$

$$|\pi_g 2p_y\rangle \propto (|2p_{y,A}\rangle - |2p_{y,B}\rangle), \tag{9.50}$$

$$|\pi_g 2p_x\rangle \propto (|2p_{x,A}\rangle - |2p_{x,B}\rangle). \tag{9.51}$$

These π MOs have one nodal planes that contain the internuclear axis as illustrated in Fig. 9.4. The bonding orbital has u symmetry and the anti-bonding has g symmetry. The axis perpendicular to the internuclear axis can be either x or y axis. Thus, there are two π MOs for each type of bonding and anti-bonding.

In general, σ interactions are stronger than π interactions because electrons are more localized along the internuclear axis for the former. Therefore, it is expected

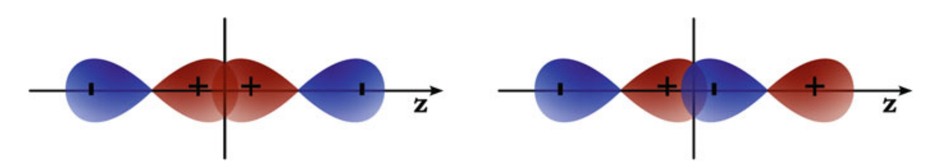


Fig. 9.3 Bonding molecular orbital, $\sigma_g 2p_z$ (left), and anti-bonding molecular orbital, $\sigma_u 2p_z$ (right), formed by two $2p_z$ atomic orbitals

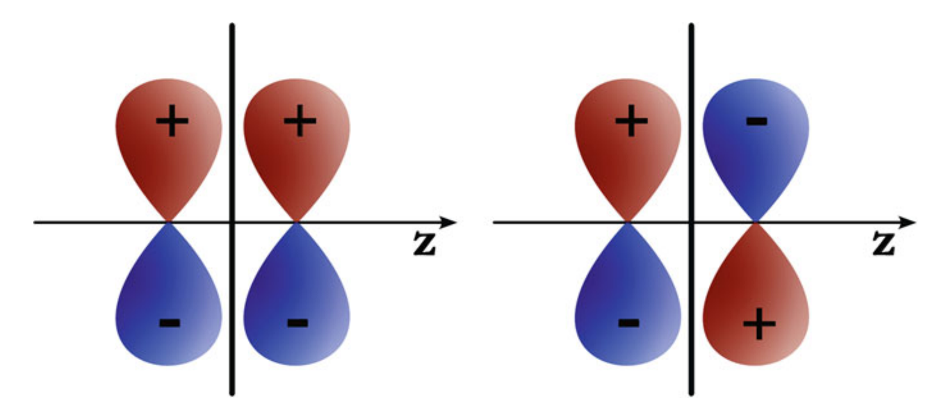


Fig. 9.4 Bonding π molecular orbital, $2\pi_u 2p$ (left), and anti-bonding π molecular orbital, $2\pi_g 2p$ (right), formed by $2p_x$ or $2p_y$ atomic orbitals

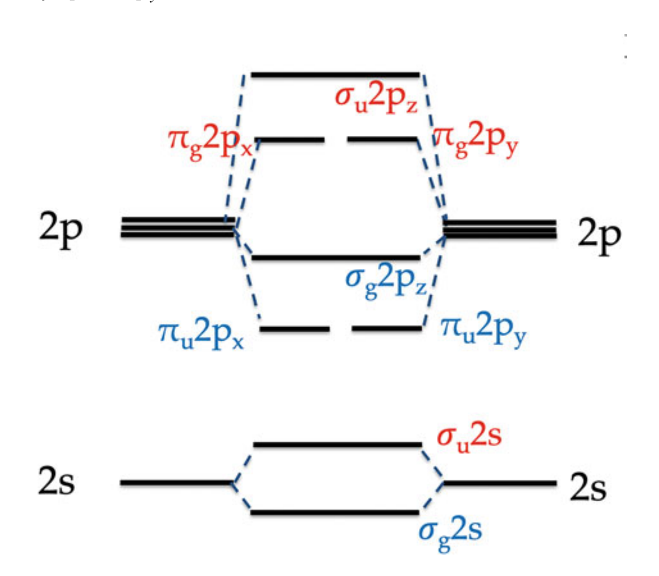


Fig. 9.5 MO diagram corresponding to Li_2 through N_2

that $\sigma_g 2p_z$ bonding orbital has lower energy than $\pi_u 2p_{x,y}$ and that $\sigma_u 2p_z$ has higher energy than $\pi_g 2p_{x,y}$. However, for diatomic molecules ranging from Li_2 through N_2, the relative order of bonding orbitals is switched. Thus, $\sigma_g 2p_z$ has higher energy than $\pi_u 2p_{x,y}$ for these molecules. This is an outcome of repulsive interactions from electrons already occupying the $\sigma_u 2s$ orbital, which destabilizes the $\sigma_g 2p_z$ orbital because they have significant overlap along the internuclear axis. Figure 9.5 shows the MO energy diagram reflecting this effect. The ground electronic configurations that are obtained by filling up electrons according to the molecular building-up principle are listed in Table 9.1.

Table 9.1 Molecular configurations, bond order, and term symbols of ground electronic states for stable diatomic molecules

	# of elec.	Configuration	B. O.	Ground st.
H_2^+	1	$(\sigma_g 1s)^1$	1/2	$^2\Sigma_g^+$
H_2	2	$(\sigma_g 1s)^2$	1	$^1\Sigma_g^+$
He_2^+	3	$(\sigma_g 1s)^2(\sigma_u 1s)^1$	1/2	$^2\Sigma_u^+$
He_2	4	$(\sigma_g 1s)^2(\sigma_u 1s)^2$	0	
Li_2	6	$KK(\sigma_g 2s)^2$	1	$^1\Sigma_g^+$
Be_2	8	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2$	0	
B_2	10	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p_{x,y})^2$	1	$^3\Sigma_g^-$
C_2	12	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p_{x,y})^4$	2	$^1\Sigma_g^+$
N_2	14	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p_{x,y})^4(\sigma_g 2p_z)^2$	3	$^1\Sigma_g^+$
O_2	16	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p_{x,y})^4(\sigma_g 2p_z)^2(\pi_g 2p_{x,y})^2$	2	$^3\Sigma_g^-$
F_2	18	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p_{x,y})^4(\sigma_g 2p_z)^2(\pi_g 2p_{x,y})^4$	1	$^1\Sigma_g^+$

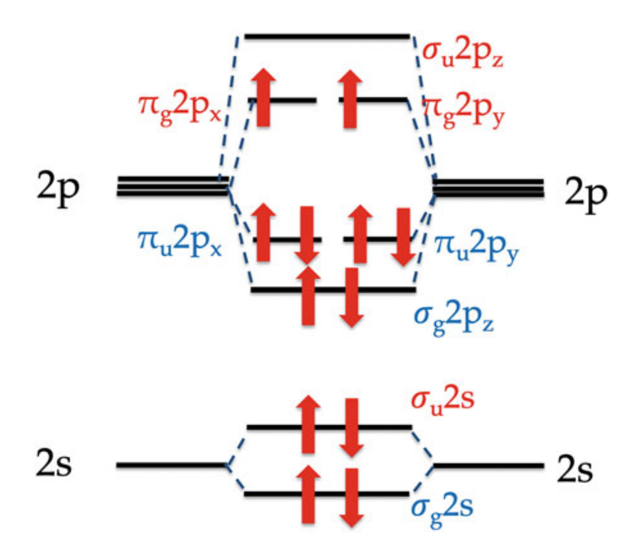


Fig. 9.6 MO diagram for O_2 and F_2. The electrons filled in represent the configuration of O_2

On the other hand, for O_2 and F_2, the original order is restored and the $\sigma_g 2p_z$ orbital has lower energy than $\pi_u 2p$ orbitals. This is because large nuclear charges of these molecules cause large enough separation of energy levels between the $\sigma_u 2s$ and $\sigma_g 2p_z$ orbitals compared to their electron-electron repulsion effect. The resulting MO diagrams, with all electrons for O_2 filled, are shown in Fig. 9.6. For the case of F_2, the additional two electrons fill up the $\pi_g 2p$ orbitals. The ground electronic configurations for these are also listed in Table 9.1.

Having defined the MOs, as depicted in Figs. 9.5 and 9.6, and identified the electronic configurations of diatomic molecules as summarized in Table 9.1, it is important to assess the validity and accuracy of the approximations involved. To this end, photoelectron spectroscopy and Koopmans' theorem play important roles, which are summarized below.

Photoelectron Spectroscopy

Photoelectron spectroscopy is the molecular version of the photoelectric effect where a photon of large enough energy is absorbed by a molecule and an electron is released from the molecule. Due to the energy conservation, the following relationship holds for a photoelectron spectroscopy:

$$\hbar \nu_{ph} = \frac{1}{2} m_e v^2 + I_i, \tag{9.52}$$

where ν_{ph} is the frequency of the photon being absorbed by the molecule, v is the speed of the ejected electron, and I_i is the ionization energy of the molecule.

Koopmans' Theorem

According to Koopmans, the ionization energy can be approximated well by the negative of the orbital energy as follows:

$$I_i \approx -\mathcal{E}_i, \tag{9.53}$$

where $\mathcal{E}_i$ is the energy of the orbital the electron is ejected from.

Combination of Eqs. (9.52) and (9.53) provide direct means to experimentally determine the energies of MOs. Indeed, these experimental results have confirmed the validity of the MOs and configurations for diatomic molecules described above. Ionization energies of molecules are typically several electron volts even for valence electrons, for which photon with wavelength less than 200 nm is typically needed.

So far, only homonuclear diatomic molecules have been considered. For heteroatomic diatomic molecules, if atomic numbers are not significantly different, similar MO levels can be used. However, even in this case, the notation g or u cannot be used any more because the molecule no longer has the inversion symmetry. The magnitudes of coefficients contributing to LCAO-MOs are different as well. Other than that, the order of MO energy levels and the building-up principle remain intact. For example, CO and CN^- have the following ground electronic configuration:

$$\mathrm{KK}(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma^* 2p_z)^2,$$

for which the B.O. is 1.

For diatomic molecules formed by those with significantly different atomic numbers, different types of MOs have to be used because only atomic orbitals with similar energies and proper symmetries form significant molecular orbitals. For example, HF has the following electronic configuration:

$$(1s_F)^2(2s_F)^2(1\sigma)^2(2p_{xF})^2(2p_{yF})^2$$

While the LCAO-MO approximation still provides simple understanding that is useful, in reality, actual MOs being formed become complicated once interactions among all the electrons and perturbation by other MOs are taken into consideration. Still, the notations for $\sigma, \pi, \cdots$ can be used since the molecules remain cylindrically symmetric. Thus, more generally, instead of specifying the atomic orbitals constituting MOs within the simplest LCAO-MO approximation, the MOs are labelled by numbers of increasing order. For example, F_2 has the following configuration:

$$(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g^*)^4$$

9.2.3 Molecular Electronic States of Diatomic Molecules

All the diatomic molecules have cylindrical symmetry, for which $\hat{L}_z$ (with the z axis defined as the direction of internuclear axis) commutes with the molecular Hamiltonian. Therefore, the eigenvalue of $\hat{L}_z$ serves as a good quantum number, and can be used to label the electronic states of all diatomic molecules. For this, Λ, the absolute value of the eigenvalue of $\hat{L}_z$ divided by $\hbar$, is used. In other words, states with Λ have $\pm\Lambda\hbar$ as eigenvalues of $\hat{L}_z$. For $\Lambda = 0$, this is a single state. For $\Lambda \neq 0$, this represents doubly degenerate states. These different states, along with other important properties, can be represented compactly by molecular term symbols that are introduced below.

Molecular Term Symbols

The following molecular term symbol is used to express the electronic states of diatomic molecules:

$$^{2S+1}\mathrm{M}^{\pm}_{g(u)},$$

where M is one of capital Greek letters, $\Sigma, \Pi, \Delta, \Gamma$ for $\Lambda = 0, 1, 2, 3$, respectively. In the left superscript, S is the total spin quantum number of electrons. In the right subscript, g is used for a state with even inversion symmetry and u is used for a state with odd inversion symmetry. In the right

(continued)

superscript, + means even reflection symmetry and − means odd reflection symmetry with respect to a plane containing the internuclear axis.

For the case of singly occupied MOs, it is easy to find the corresponding term symbols because the state has the same symmetry as the MO and the spin multiplicity is always 2. Below are examples:

$$(\sigma_g)^1 \rightarrow {}^2\Sigma_g^+$$
$$(\sigma_u)^1 \rightarrow {}^2\Sigma_u^+$$
$$(\pi_u)^1 \rightarrow {}^2\Pi_u$$
$$(\pi_g)^1 \rightarrow {}^2\Pi_g$$

For the case of fully occupied MOs, the spin multiplicity is 1 and the electronic state is totally symmetric. Thus, all of $(\sigma_g)^2$, $(\sigma_u)^2$, $(\pi_g)^4$, and $(\pi_u)^4$ have the same term, ${}^1\Sigma_g^+$. For the case of one less than fully filled MOs, the term is the same as singly occupied MOs. This is because, the former can be viewed as that of a single hole (absence of electron) which has to obey the same property as the electron as far as the molecular term symbols are concerned.

For the case where two electrons occupy the same orbitals, for example, as in $(\pi_g)^2$ or $(\pi_u)^2$, care should be taken in identifying all possible term symbols that are consistent with the Pauli principle. A simple way to figure out all possible terms is to consider the sum of the pair of single electron angular momentum and spin values, l_z and s_z. For example, for an electron occupying the π molecular orbital, the following four pairs exist.

$$a : \left(1, \frac{1}{2}\right) \qquad b : \left(-1, \frac{1}{2}\right)$$
$$a' : \left(1, -\frac{1}{2}\right) \qquad b' : \left(-1, -\frac{1}{2}\right)$$

Then, all possible values for the total L_z and S_z of the two electrons occupying the π orbitals can be found by summing all distinctive pairs of (l_z, s_z). Considering only the positive values of these, we obtain the following four cases of (Λ, S):

$$a + a' : (2, 0) \qquad a + b : (0, 1)$$
$$a + b' : (0, 0)$$
$$a' + b : (0, 0)$$

In the above list, the case with $\Lambda = 2$ and $S = 0$ corresponds to a term with $^1\Delta_g$. Here, the subscript g is used because two electrons occupying the same orbital always have even symmetry with respect to inversion regardless of the symmetry of individual MOs. In the remaining three pairs, (0, 1) and (0, 0) represent the case with $\Lambda = 0$ and $S = 1$. These apparently represent triplet states. For this to be true, the MO should be an antisymmetric combination of the product of two single electron π orbitals, which is expected to have odd reflection symmetry with respect to a plane containing an internuclear axis. Therefore, these correspond to $^3\Sigma_g^-$. The remaining pair corresponds to the case of $\Lambda = 0$ and $S = 0$. Since the spin state is antisymmetric, the orbital in this case has to be a symmetric combination of two atomic π orbitals, for which the reflection symmetry with respect to a plan containing the internuclear axis is even. Therefore, this corresponds to $^1\Sigma_g^+$.

Compiling all the results obtained so far, we find that both $(\pi_g)^2$ and $(\pi_u)^2$ have the following three different terms:

$$^3\Sigma_g^-,\ ^1\Delta_g,\ ^1\Sigma_g^+.$$

Note that the terms above are listed in the order of increasing energy according to Hund's rules.[6] In other words, the states with higher spin multiplicity have lower energies. Among the states with the same spin multiplicity, the states with the higher value of Λ have lower energies.

For two electrons in two different orbitals, all possible combinations of Λ and S can be used without restriction. For example, for an excited configuration of H_2, $(1\sigma_g)^1(1\sigma_u)^1$, the following two terms exist:

$$^3\Sigma_u^+,\ ^1\Sigma_u^+,$$

where the two terms are listed in the order of increasing order of energy according to Hund's rules. For an excited state configuration of N_2, $(1\pi_u)^3(3\sigma_g)^2(1\pi_g^*)^1$, there are four possible terms, and they can be written in the order of increasing energy according to Hund's rules as follows:

$$^3\Delta_u,\ ^3\Sigma_u^\pm,\ ^1\Delta_u,\ ^1\Sigma_u^\pm.$$

Transitions between the electronic states of diatomic molecules due to absorption or emission of a single photon occur according to well known selection rules. More generally, one can identify a set of selection rules for electronic states of linear molecules as described below.

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[6] For molecular electronic states, Hund's rules are less reliable than atomic electronic states.

Selection Rules for Electronic Transitions of Linear Molecules

- $\Delta\Lambda = 0, \pm 1$: This is because the total orbital angular momentum number of all electrons L can change only by ± 1 or remain the same, for which Λ can change only by ± 1 at most or remain the same.
- $\Delta S = 0$: This is because the spectroscopy involves interaction of the electric filed part of the radiation, which does not interaction with spins and thus leaves the total spin of electrons intact.
- There is no transition between Σ^+ and Σ^- states: This is because the transition dipole moment interacting with the radiation is always along the direction of the internuclear axis due to the cylindrical symmetry. This means that the transition dipole has positive reflection symmetry and thus cannot couple any two states with different reflection symmetries.
- Only transitions between u and g symmetries are allowed: In other words, transition between states with the same inversion symmetries is not allowed. This is because the transition dipole has u symmetry and thus can couple only states with different inversion symmetries.

9.3 Conjugated Hydrocarbons and Hückel Approximation

The simple LCAO-MO approximation can be useful for qualitative understanding of π-type electronic states formed by p_z orbitals in hydrocarbons with conjugated double bonds. In fact, one can make further simplifications known as Hückel approximation as described below.

Hückel Approximation

For π-type molecular orbitals formed by p_z orbitals (p orbitals perpendicular to $C-C$ bonding), the following three approximations can be made.

- All the overlap integrals between different p_z orbitals are zero.
- All the diagonal elements of the electronic Hamiltonian with respect to p_z orbitals are assumed to be the same as follows:

$$H_{ii} = \langle 2p_{zi}|\hat{H}_{en}|2p_{zi}\rangle = \alpha. \tag{9.54}$$

- All the off-diagonal elements of the electronic Hamiltonian between different p_z orbitals are assumed to be zero except for those due to the

(continued)

nearest neighbors, which are also assumed to be the same as follows:

$$H_{ii+1} = \langle 2p_{zi}|\hat{H}_{en}|2p_{zi+1}\rangle = \langle 2p_{zi+1}|\hat{H}_{en}|2p_{zi}\rangle = \beta. \tag{9.55}$$

9.3.1 Ethylene

As the simplest example, let us consider ethylene, for which the π-type LCAO-MO formed by the two p_z orbitals can be expressed as

$$|\psi_\pi\rangle = C_1|2p_{z1}\rangle + C_2|2p_{z2}\rangle. \tag{9.56}$$

Application of the variational principle described in Chap. 7 for the above state leads to the following matrix equation:

$$\begin{pmatrix} H_{11} - E & H_{12} - ES_{12}. \\ H_{12} - ES_{12} & H_{22} - E \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}, \tag{9.57}$$

where $H_{11} = \langle p_{z1}|\hat{H}_{en}|p_{z1}\rangle$, $H_{22} = \langle p_{z2}|\hat{H}_{en}|p_{z2}\rangle$, $\hat{H}_{12} = \langle p_{z1}|\hat{H}_{en}|p_{z2}\rangle$, and $S_{12} = \langle p_{z1}|p_{z2}\rangle$. Based on the Hückel approximation, $H_{11} = H_{22} = \alpha$ and $H_{12} = \beta$, Thus, the above matrix equation implies that

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = (\alpha - E)^2 - \beta^2 = (\alpha - E - \beta)(\alpha - E + \beta) = 0. \tag{9.58}$$

Therefore, there are two possible solutions, $E = \alpha \pm \beta$.

For the case of $E = \alpha + \beta$, solving Eq. (9.57) results in

$$-\beta C_1 + \beta C_2 = 0. \tag{9.59}$$

This, along with the normalization condition, means that $C_1 = C_2 = 1/\sqrt{2}$. For the case of $E = \alpha - \beta$, solving Eq. (9.57) results in

$$\beta C_1 + \beta C_2 = 0. \tag{9.60}$$

This, along with the normalization condition, means that $C_1 = -C_2 = 1/\sqrt{2}$. These results for ethylene are summarized below.

π Molecular Orbitals and Energies for Ethylene

The π bonding and π^* anti-bonding states for ethylene and their energies are as follows:

$$|\psi_\pi\rangle = \frac{1}{\sqrt{2}}\left(|2p_{z1}\rangle + |2p_{z2}\rangle\right), \; E_\pi = \alpha + \beta \tag{9.61}$$

$$|\psi_{\pi^*}\rangle = \frac{1}{\sqrt{2}}\left(|2p_{z1}\rangle - |2p_{z2}\rangle\right), \; E_{\pi^*} = \alpha - \beta \tag{9.62}$$

9.3.2 Butadiene

As the next example, let us consider butadiene. For this case, the π −MO constructed from the linear combination of four p_z orbitals is expressed as

$$|\psi_\pi\rangle = C_1|2p_{z1}\rangle + C_2|2p_{z2}\rangle + C_3|2p_{z3}\rangle + C_4|2p_{z4}\rangle. \tag{9.63}$$

Then, application of the variational principle and Hückel approximation leads to the following equation for E and the C_k:

$$\begin{pmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}. \tag{9.64}$$

Let us introduce

$$x = \frac{\alpha - E}{\beta}. \tag{9.65}$$

Then, the above matrix equation can be equivalently expressed as

$$\begin{pmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}. \tag{9.66}$$

This implies that

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = x \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} - \begin{vmatrix} 1 & 1 & 0 \\ 0 & x & 1 \\ 0 & 1 & x \end{vmatrix} = x(x^3 - 2x) - (x^2 - 1) = x^4 - 3x^2 + 1 = 0. \tag{9.67}$$

Solving the above algebraic equation, we obtain

$$x^2 = \frac{3 \pm \sqrt{5}}{2} = \left(\frac{\sqrt{5} \pm 1}{2} \right)^2, \tag{9.68}$$

which correspond to the following solutions for x:

$$x = \frac{\sqrt{5}+1}{2}, \frac{\sqrt{5}-1}{2}, -\frac{\sqrt{5}-1}{2}, -\frac{\sqrt{5}+1}{2}. \tag{9.69}$$

Since $x = (\alpha - E)/\beta$, the above solutions correspond to the following four values for the energies:

$$E = \alpha - \frac{\sqrt{5}+1}{2}\beta, \alpha - \frac{\sqrt{5}-1}{2}\beta, \alpha + \frac{\sqrt{5}-1}{2}\beta, \alpha + \frac{\sqrt{5}+1}{2}\beta. \tag{9.70}$$

Since β is negative, the energies given above are in the decreasing order.

Employing the corresponding value of x for each case in Eq. (9.66), we can obtain the corresponding MOs. For this, it is useful to rearrange the linear equations for C_k's. First, note that Eq. (9.64) is equivalent to the following equations:

$$C_1 x + C_2 = 0, \tag{9.71}$$

$$C_1 + xC_2 + C_3 = 0, \tag{9.72}$$

$$C_2 + xC_3 + C_4 = 0, \tag{9.73}$$

$$C_3 + C_4 x = 0. \tag{9.74}$$

Adding Eqs. (9.72) and (9.73), we obtain

$$C_1 + (1+x)C_2 + (1+x)C_3 + C_4 = 0. \tag{9.75}$$

Subtracting Eq. (9.73) from Eq. (9.72), we also obtain

$$C_1 + (x-1)C_2 + (1-x)C_3 - C_4 = 0. \tag{9.76}$$

From Eqs. (9.71) and (9.74), we find that $C_2 = -xC_1$ and $C_3 = -xC_4$. Substituting these for C_2 and C_3 in Eqs. (9.75) and (9.76), we obtain the following two different equations involving C_1 and C_4.

$$C_1(1 - x - x^2) + C_4(1 - x - x^2) = 0, \tag{9.77}$$

$$C_1(1 + x - x^2) - C_4(1 + x - x^2) = 0. \tag{9.78}$$

For the cases of $x = (\sqrt{5} + 1)/2$ and $x = -(\sqrt{5} - 1)/2$, $1 + x - x^2 = 0$ and Eq. (9.78) is already satisfied. Therefore, using Eq. (9.77), we find that $C_1 = -C_4$. On the other hand, for the cases of $x = (\sqrt{5} - 1)/2$ and $x = -(\sqrt{5} + 1)/2$, $1 - x - x^2 = 0$ and Eq. (9.77) is already satisfied. Therefore, using Eq. (9.78), we find that $C_1 = C_4$. As a result, we obtain the following four MOs corresponding to the four values of the energy for butadiene.

π-MO Energies and States for Butadiene

π-MO energies and states formed by linear combinations of p_z orbitals, indexed in an increasing order of energy, are provided below.

	E_π	$\lvert\psi_{\pi-\mathrm{MO}}\rangle$
1	$\alpha + \frac{\sqrt{5}+1}{2}\beta$	$C_1\left(\lvert 2p_{z1}\rangle + \frac{\sqrt{5}+1}{2}\lvert 2p_{z2}\rangle + \frac{\sqrt{5}+1}{2}\lvert 2p_{z3}\rangle + \lvert 2p_{z4}\rangle\right)$
2	$\alpha + \frac{\sqrt{5}-1}{2}\beta$	$C_1\left(\lvert 2p_{z1}\rangle + \frac{\sqrt{5}-1}{2}\lvert 2p_{z2}\rangle - \frac{\sqrt{5}-1}{2}\lvert 2p_{z3}\rangle - \lvert 2p_{z4}\rangle\right)$
3	$\alpha - \frac{\sqrt{5}-1}{2}\beta$	$C_1\left(\lvert 2p_{z1}\rangle - \frac{\sqrt{5}-1}{2}\lvert 2p_{z2}\rangle - \frac{\sqrt{5}-1}{2}\lvert 2p_{z3}\rangle + \lvert 2p_{z4}\rangle\right)$
4	$\alpha - \frac{\sqrt{5}+1}{2}\beta$	$C_1\left(\lvert 2p_{z1}\rangle - \frac{\sqrt{5}+1}{2}\lvert 2p_{z2}\rangle + \frac{\sqrt{5}+1}{2}\lvert 2p_{z3}\rangle - \lvert 2p_{z4}\rangle\right)$

The values of C_1 in above expressions can be determined by the normalization condition. For states 1 and 4, $C_1 = 1/\sqrt{5 + \sqrt{5}}$. For states 2 and 3, $C_1 = 1/\sqrt{5 - \sqrt{5}}$.

9.3.3 π Orbital and Delocalization Energies

Having obtained the π-MOs, let us now consider the π orbital energies of electrons within the independent electron model. The ground electronic state is obtained by filling in two electrons from the lowest possible π-MOs.

For the case of ethylene, the two valance electrons from p_z atomic orbitals can fill the lowest energy π-MO with energy $\alpha + \beta$. Thus, the π orbital energy for ethylene is

$$E_\pi(\text{ethylene}) = 2(\alpha + \beta) = 2\alpha + 2\beta. \tag{9.79}$$

On the other hand, for butadiene, there are four valance electrons coming from p_z atomic orbitals. These can fill in the two lowest energy π-MOs, for which the energy is equal to

$$\begin{aligned} E_\pi(\text{butadiene}) &= 2\left(\alpha + \frac{\sqrt{5}+1}{2}\beta\right) + 2\left(\alpha + \frac{\sqrt{5}-1}{2}\beta\right) \\ &= 4\alpha + 2\sqrt{5}\beta. \end{aligned} \tag{9.80}$$

Note that the π orbital energy for butadiene is different from twice the π electron energies of ethylene. The difference between the two accounts for the additional stabilization due to conjugation (or delocalization) of neighboring π-MOs and accounts for the stability of π-conjugated molecules as summarized below.

π-Bonding Delocalization (or Conjugation) Energy

The π bonding delocalization energy is the difference of the total π-orbital energy from the sum of those for isoelectronic ethylenes. For the case of butadiene,

$$E_{\pi-\text{del}}(\text{butadiene}) = 4\alpha + 2\sqrt{5}\beta - 4(\alpha + \beta) = 2(\sqrt{5} - 2)\beta. \tag{9.81}$$

9.4 Molecular Symmetry and Group Theory

9.4.1 Symmetry and Symmetry Operation

Symmetry plays an important role in quantum mechanics. It allows determination of the nature of eigenstates of the Hamiltonian and classifying them without going through detailed calculations. For molecular systems, consideration of symmetry in particular enables constructing MOs in an efficient manner and identifying the nature of vibrational modes, both with the help of the group theory [9–13]. We begin this section with more exact definition of symmetry and related terms as listed below.

Symmetry and Related Terms

- **Symmetry**: An object is called to have *symmetry* if it remains equivalent (appears to look the same) after certain operation.
- **Symmetry operation**: An operation that is intended to test whether an object has symmetry or not is called *symmetry operation*.
- **Symmetry element**: A geometrical object with respect to which a symmetry operation is performed.

The two definitions of *symmetry* and *symmetry operation* seem somewhat circular, but it is important to note that the former is the property of a specific object whereas the latter can be applied to any object. Thus, a symmetry operation can be defined independent of objects it is being applied to. It only requires existence of a *symmetry element* with respect which the operation is performed.

Symmetry operation is also a physically well-defined operation, which can also be viewed as a quantum mechanical operator with proper definition of its action on either physical observables or states. The fact that a molecule has certain symmetry is equivalent to stating that the Hamiltonian for the molecule commutes with the corresponding quantum mechanical symmetry operator. This important fact will be detailed further later. In many cases, the same symbol is used for symmetry operator and symmetry element, which often becomes the source of confusion between the two. Therefore, operator notation is used here for the symmetry operation.

Out of all possible symmetry operations, we will focus here only on *point symmetry operations*, which leave at least one point of the object being operated on unchanged. Point symmetry operations are the only kinds of operations needed for the specification of intrinsic properties of molecules. Let us first review the basic types of point symmetry operations as listed below.

Point Symmetry Operations

There are five types of symmetry operations [9] that form the basis for all point symmetry operations as listed below.

- **Identity operation**, $\hat{E}$, is doing nothing, and does not have any symmetry element associated with it.
- **Inversion operation**, $\hat{i}$, is an inversion with respect to an *inversion center*. If the inversion center is origin, this operator transforms (x, y, z) to $(-x, -y, -z)$. Application of this operation twice becomes the identity operation as follows: $\hat{i}^2 = \hat{i} \cdot \hat{i} = \hat{E}$.

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- **Proper rotation**, $\hat{C}_n$, is an operation that rotates around an axis (denoted as C_n axis) by $2\pi/n$ and is called n-fold proper rotation operation. Note that applying this operator n times leads to the identity operation as follows:

$$\left(\hat{C}_n\right)^n = \underbrace{\hat{C}_n \cdot \hat{C}_n \cdot \cdots \hat{C}_n}_{n \text{ times}} = \hat{E}$$

- **Reflection operator**, $\hat{\sigma}$, reflects a point or body with respect to a plane of reflection. For example, if the plane of reflection is the xy-plane, this operation transforms a point (x, y, z) to $(x, y, -z)$. If the plane of reflection is yz-plane, the operation transforms a point (x, y, z) to $(-x, y, z)$. When both $\hat{C}_n$'s and $\hat{\sigma}$'s coexist in a group of symmetry operations, the reflection plane that contains C_n axis with the highest value of n is denoted as σ_v. On the other hand, the plane perpendicular to C_n is denoted as σ_h.
- **Improper rotation**, $\hat{S}_n$, is a combination of a proper rotation and a reflection with respect to σ_h, the plane perpendicular to the proper rotation axis C_n. Thus, $\hat{S}_n = \hat{\sigma}_h \hat{C}_n = \hat{C}_n \hat{\sigma}_h$. Note that the two operators $\hat{\sigma}_h$ and $\hat{C}_n$ commute with each other. The symmetry element of the improper rotation is denoted as S_n, which is in fact the same as C_n. If S_n is equal to the z-axis, this operation transforms a point (x, y, z) to $(x', y', -z)$, where $x' = \cos(2\pi/n)x - \sin(2\pi/n)y$ and $y' = \sin(2\pi/n)x + \cos(2\pi/n)y$. This operation transforms every point except the origin where C_n axis and σ_h intersects. There are a few important properties of $\hat{S}_n$. Application of improper rotation twice is equal to that of proper rotation as follows: $\hat{S}_n \cdot \hat{S}_n = \hat{\sigma}_h^2 \cdot \hat{C}_n^2 = \hat{C}_n^2$. This is because $\hat{C}_n$ and $\hat{\sigma}_h$ commute with each other. Therefore, if n is even, $\hat{S}_n^n = \hat{E}$. On the other hand, if n is odd, $\hat{S}_n^n = \hat{\sigma}_h$. It is also important to note that $\hat{S}_2 = \hat{i}$. Therefore, the smallest value of n for $\hat{S}_n$, which is distinctive from others, is $n = 3$.

9.4.2 *Group Theory*

Mathematically, a group is defined by a set of group elements, which can be finite or infinite, and a rule of mapping called group multiplication, which combines any pair of group elements and produces another one [9, 10].

Definition of Group

Let us denote group elements of a group $\mathcal{G}$ as A, B, C, $\cdots$, and the group multiplication as $\circ$. Then, the set of elements and the multiplication constituting $\mathcal{G}$ should satisfy the four properties described below.

1. If A and B are elements of $\mathcal{G}$, then $A \circ B$ and $B \circ A$ are also elements of $\mathcal{G}$.
2. There is an identity element E in the group such that $A \circ E = E \circ A = A$ for any A in $\mathcal{G}$.
3. The group multiplication $\circ$ is associative. In other words, $(A \circ B) \circ C = A \circ (B \circ C)$ for any A, B, and C in $\mathcal{G}$. Note that the multiplication does not have to be commutative. In other words, $A \circ B$ does not the have to be the same as $B \circ A$. In case the group multiplications are commutative for all elements of a group, such a group is called an Abelian group.
4. For any group element A in the group $\mathcal{G}$, there is always a unique inverse of A, which is denoted as A^{-1}, such that $A \circ A^{-1} = A^{-1} \circ A = E$.

There are various finite and infinite groups. For example, the set of integers can be shown to be a group by defining addition (+) as the group multiplication. A well-known finite group is the set of integers mod n (remainder after division), where n is an arbitrary positive integer. The group multiplication in this case is defined as the sum of two integers mod n. For example, for $n = 3$, the group elements are 0, 1, and 2, and the results of group multiplications of these elements are as follows: $0 \circ 1 = 1 \circ 0 = 1$, $0 \circ 2 = 2 \circ 0 = 2$, $1 \circ 2 = 2 \circ 1 = 0$. Thus, 0 is the identity element for this group, and the inverse of 1 (2) is 2 (1). Both of these groups are Abelian groups.

Important Terms and Concepts in Group Theory

- **Order**, is the total number of elements of a group, which will be denoted as Q here, and can be either finite or infinite.
- **Group multiplication table**, is a $Q \times Q$ table that specifies the results of the group multiplication of all pairs of group elements.
- **Conjugate elements**: Two elements A and A' of a group are called conjugate if they are related by the following similarity transformation: $A' = B \circ A \circ B^{-1}$, where B is any element in the group and B^{-1} is its inverse. If this relationship holds, $A' \circ B = B \circ A$.
- **Class**: The set of all conjugate elements in a group is called a class. For an Abelian group, each element forms its own class since $A \circ B = B \circ A$ for any A and B.

(continued)

- **Representation**, refers to any group composed of concrete mathematical entities that are homomorphic (many-to-one mapping from represented elements to the original group element) or isomorphic (one-to-one mapping) to the original abstract group that can be completely specified by the group multiplication table.
- **Matrix representation**, is the representation where each group element is represented by a square matrix and the group multiplication is the matrix multiplication.
- **Equivalent matrix representations**: Two matrix representations $\mathbf{\Gamma}'$ and $\mathbf{\Gamma}$ of a group are called equivalent if there is an invertible matrix $\mathbf{S}$ relating the two for all matrix representations of the group as follows:

$$\mathbf{\Gamma}'(A_i) = \mathbf{S}^{-1}\mathbf{\Gamma}(A_i)\mathbf{S}, \text{ for } i = 1, \cdots, Q , \tag{9.82}$$

where A_i's represent all the elements of the group with order Q.

9.4.3 Groups of Point Symmetry Operations

Certain sets of point symmetry operations can form group. In a group of point symmetry operations, the group elements are symmetry operations and the group multiplication of two "elements" is defined as successive application of the two operations, with the convention that the one on the righthand side is always applied first. These groups can be classified according to what symmetry operations generate the entire elements of a group and are listed in the Table 9.2, employing Schönflies notation. For example, the group C_{nv} consists of $\hat{E}$, $\hat{C}_n$, and n different σ_v's and all others that can be generated from them such as $\hat{C}_n^k$ with $k = 2, \cdots, n-1$.

In Table 9.2, note that there are no S_{2n-1} points groups. The reason for this is as follows [9]. If there were a group called S_{2n-1}, it should be generated by the corresponding improper rotation operation $\hat{S}_{2n-1}$. This means that such a group also should have $\hat{S}_{2n-1}^{2n-1} = \hat{\sigma}_h$, which also implies that it should have $\hat{C}_{2n-1} = \hat{\sigma}_h \hat{S}_{2n-1}$ as its group element. However, such a group has already been classified as the C_{2n-1h} group. Since we do not want duplicate notations for the same group, the customary practice is to assume that only S_{2n} groups exist.

The groups from T to I_h in Table 9.2 are called cubic point groups. Among these point groups, T_d, T_h, O_h, and I_h exactly have the same symmetries of tetrahedron, cube, octahedron, and icosahedron, respectively.

Typically, it is stated that *a given molecule belongs to a certain point group* if its structure (in the ground electronic state) remains *unchanged with respect to all the symmetry operations constituting the point group*. For example, it is easy to show that H_2O belongs to the C_{2v} point group and benzene C_6H_6 belongs to the point

Table 9.2 Point groups and their respective generating operators. Except for the first three point groups, where all the generators form a complete group, there are additional symmetry operators being generated by those listed, which altogether form a complete set of symmetry operations

Point group	Generating operators
C_1	$\hat{E}$ (complete)
C_s	$\hat{E}$, $\hat{\sigma}$ (complete)
C_i	$\hat{E}$, $\hat{i}$ (complete)
C_n	$\hat{E}$, $\hat{C}_n$
C_{nv}	$\hat{E}$, $\hat{C}_n$, n different $\hat{\sigma}_v$'s
C_{nh}	$\hat{E}$, $\hat{C}_n$, $\hat{\sigma}_h$
D_n	$\hat{E}$, $\hat{C}_n$, n different $\hat{C}_2$'s (perpendicular to $\hat{C}_n$)
D_{nh}	$\hat{E}$, $\hat{C}_n$, n different $\hat{C}_2$'s (perpendicular to $\hat{C}_n$), $\hat{\sigma}_h$
D_{nd}	$\hat{E}$, $\hat{C}_n$, n different $\hat{C}_2$'s (perpendicular to $\hat{C}_n$), n $\hat{\sigma}_d$'s
S_{2n}	$\hat{E}$, $\hat{S}_{2n}$
$C_{\infty v}$	C_{nv} in the limit of $n \to \infty$
$D_{\infty h}$	D_{nh} in the limit of $n \to \infty$
T	$\hat{E}$, three perpendicular $\hat{C}_2$'s, and four C_3's
T_d (tetrahedron)	$\hat{E}$, three perpendicular $\hat{C}_2$'s, four C_3's, six $\hat{\sigma}_d$'s
v T_h (cube)	$\hat{E}$, three perpendicular $\hat{C}_2$'s, four C_3's, $\hat{i}$
O	$\hat{E}$, two sets of three perpendicular $\hat{C}_4$'s, eight C_3's
O_h (octahedron)	$\hat{E}$, two sets of three perpendicular $\hat{C}_4$'s, eight C_3's, $\hat{i}$
I	$\hat{E}$, four sets of three perpendicular $\hat{C}_5$'s, twenty C_3's
I_h (icosahedron)	$\hat{E}$, four sets of three perpendicular $\hat{C}_5$'s, twenty C_3's, $\hat{i}$

group D_{6h}. If this is the case, The importance of the point group of a given molecule is that the Hamiltonian within the BO approximation, Eq. (9.18), commutes with all the symmetry operations of the group, which also means that it is possible to determine simultaneous eigenstates of both the Hamiltonian and all the symmetry operators of the group. This can be used to identify symmetry adapted LCAO-MOs and also for identifying IR and Raman activity of molecular vibrational modes.

If a molecule is polar, it belongs to only one of C_n, C_s, and C_{nv}. This is because a given polar molecule should have nonzero permanent dipole moment. Since the permanent dipole should be invariant with respect to all the symmetry operations constituting the group that the molecule belongs to, the dipole vector should be contained in the intersection of all symmetry elements defining the group operations. This is possible only if all symmetry operations share at least one line on which the permanent dipole vector lies. For this to be true, there should be no inversion center or planes perpendicular to C_n. The three groups listed above are the only such groups having this property.

9.4.4 Matrix Representation of Point Symmetry Group Elements

For groups consisting of point symmetry operations, representation of each group element (symmetry operation) by a square matrix is a convenient choice. Different matrix representations are possible depending on the choice of the basis set, but there are certain quantities that remain invariant and play important roles for defining more universal properties. One such quantity is called *character* of the matrix representation.

Character

The **character** of a matrix representation, which is denoted as χ here, refers to the trace, namely, the sum of all the diagonal matrix elements, of the matrix. The characters of two matrix representations are always the same if they are related by a unitary transformation.

For example, let us consider a basis consisting of three cartesian coordinates. Then, the symmetry operations $\hat{E}$, $\hat{C}_2$, $\hat{\sigma}_v$, and $\hat{\sigma}_v'$ constituting the C_{2v} point group can be represented as follows:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \xrightarrow{\hat{E}} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \underbrace{\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}}_{\hat{E}} \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \tag{9.83}$$

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \xrightarrow{\hat{C}_2} \begin{pmatrix} -x \\ -y \\ z \end{pmatrix} = \underbrace{\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}}_{\hat{C}_2} \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \tag{9.84}$$

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \xrightarrow{\hat{\sigma}_v} \begin{pmatrix} x \\ -y \\ z \end{pmatrix} = \underbrace{\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}}_{\hat{\sigma}_v} \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \tag{9.85}$$

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \xrightarrow{\hat{\sigma}_v'} \begin{pmatrix} -x \\ y \\ z \end{pmatrix} = \underbrace{\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}}_{\hat{\sigma}_v} \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \tag{9.86}$$

For the matrix representations of the four symmetry operations constituting the C_{2v} group, the characters are as follows: $\chi(\hat{E}) = 3$, $\chi(\hat{C}_2) = -1$, $\chi(\hat{\sigma}_v) = 1$, and $\chi(\hat{\sigma}_v') = 1$.

Note that all the four matrix representations for the above C_{2v} group are diagonal, which means that they can be represented by the properties of each one dimensional component. The matrices shown are examples of reducible representation and each of x, y, and z components here are considered as irreducible representations. More exact definitions of these are provided below.

Reducible and Irreducible Representations

- A given matrix representation of a group is called *reducible* if all the matrices representing the symmetry operations of the group can be reduced to smaller block diagonal or fully diagonal forms by the same similarity transformation, which means that there exists an invertible matrix $\hat{S}$ such that for any $\hat{A}$ in the group, $\hat{A}' = \hat{S}\hat{A}\hat{S}^{-1}$, where $\hat{S}^{-1}$ is the inverse of $\hat{S}$, becomes a matrix consisting of smaller diagonal blocks.
- A representation is called *irreducible* if all the matrices cannot be reduced to smaller block diagonal or fully diagonal forms by any similarity transformation.
- For a given point group, there is a unique set of all distinct irreducible representations.

Each irreducible representation can be fully characterized by the set of characters of symmetry operations constituting a group. For example, for the representation of the C_{2v} group shown above, each component x, y, and z corresponds to an irreducible representation with the following characters.

	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}_v'$	Irrep.
x	1	-1	1	-1	B_1
y	1	-1	-1	1	B_2
z	1	1	1	1	A_1

In the above table, the right column shows the conventional notation for the three one dimensional irreducible representations. A fairly complete description of notations for irreducible representations is provided below.

Notations for Irreducible (Irrep.) Representations

The main symbols denoting the irreducible representations of finite point groups are A, B, E, and T. Each of these symbols is described below.

- A: One dimensional and symmetric with respect to $\hat{C}_n$ of the highest n.
- B: One dimensional and antisymmetric with respect to $\hat{C}_n$ of the highest n.
- E: Two dimensional.
- T: Three dimensional.

Each symbol can further classified with subscripts as described below.

- 1 (subscript): Symmetric with respect to the $\hat{C}_2$'s around C_2 axes that are perpendicular to C_n of the highest n or σ_v's.
- 2 (subscript): Antisymmetric with respect to the $\hat{C}_2$'s around C_2 axes that are perpendicular to C_n of the highest n or σ_v's.
- g (subscript): Even inversion symmetry when there is $\hat{i}$ operator in the group.
- u (subscript): Odd inversion symmetry when there is $\hat{i}$ operator in the group.

In case the group has $\hat{\sigma}_h$ operation, each Irrep. is labeled with $'$ or $''$ as follows.

- $'$: Symmetric with respect to $\hat{\sigma}_h$.
- $''$: Antisymmetric with respect to $\hat{\sigma}_h$.

Having introduced the notations for irreducible representations as detailed above, it is now possible to appreciate the implications of a character table for a point group. Let us consider, for example, the full character table for C_{2v} as follows:

C_{2v}	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$	
A_1	1	1	1	1	z, x^2, y^2, z^2
A_2	1	1	-1	-1	xy, R_z
B_2	1	-1	1	-1	x, xz, R_y
B_2	1	-1	-1	1	y, yz, R_x

Each row in the above table represents a one dimensional irreducible representation, for which only ± 1 is possible as the character. The value $1(-1)$ implies that the representation is symmetric (antisymmetric) with respect to the symmetry operation. The right column shows linear or quadratic functions of Cartesian coordinates that have the same symmetry as the given irreducible representation. R_x, R_y, and R_z represent rotations around x, y, and z axes.

In the above table for the C_{2v} point group, the number of irreducible representations is the same as the order of the group, $Q = 4$. This is because each element belongs to a different class and all irreducible representations are one dimensional. This is not always the case. For example, let us consider the C_{3v} group, which consists of the following symmetry operations:

$$\hat{E}, \hat{C}_3, \hat{C}_3^2, \hat{\sigma}_v^{(1)}, \hat{\sigma}_v^{(2)}, \hat{\sigma}_v^{(3)}.$$

In the above list, $\hat{C}_3$ and $\hat{C}_3^2$ are related to each other, forming a class, and so do the three reflection operations $\hat{\sigma}_v^{(1)}$, $\hat{\sigma}_v^{(2)}$ and $\hat{\sigma}_v^{(3)}$, which forms another class. Symmetry operations belonging to the same class have same values of characters for all the irreducible representations and thus can be grouped together in the character table. In other words, the character table for the C_{3v} group can be expressed as follows:

C_{3v}	$\hat{E}$	$2\hat{C}_3$	$3\hat{\sigma}_v$	
A_1	1	1	1	z, x^2, y^2, z^2
A_2	1	1	-1	R_z
E	2	-1	0	$(x, y), (x^2 - y^2, xy), (xz, yz), (R_x, R_y)$

In the above character table for C_{3v} point group, there is a two dimensional irreducible representation, E. All the characters of this can be confirmed by considering how the two dimensional x and y coordinates are transformed as follows:

$$\begin{pmatrix} x \\ y \end{pmatrix} \xrightarrow{\hat{C}_3} \begin{pmatrix} \cos(2\pi/3)x - \sin(2\pi/3)y \\ \sin(2\pi/3)x + \cos(2\pi/3)y \end{pmatrix} = \underbrace{\begin{pmatrix} \cos(2\pi/3) & -\sin(2\pi/3) \\ \sin(2\pi/3) & \cos(2\pi/3) \end{pmatrix}}_{\hat{C}_3} \begin{pmatrix} x \\ y \end{pmatrix},$$

$$\begin{pmatrix} x \\ y \end{pmatrix} \xrightarrow{\hat{C}_3^2} \begin{pmatrix} \cos(4\pi/3)x - \sin(4\pi/3)y \\ \sin(4\pi/3)x + \cos(4\pi/3)y \end{pmatrix} = \underbrace{\begin{pmatrix} \cos(4\pi/3) & -\sin(4\pi/3) \\ \sin(4\pi/3) & \cos(4\pi/3) \end{pmatrix}}_{\hat{C}_3^2} \begin{pmatrix} x \\ y \end{pmatrix},$$

$$\begin{pmatrix} x \\ y \end{pmatrix} \xrightarrow{\hat{\sigma}_v^{(1)}} \begin{pmatrix} x \\ -y \end{pmatrix} = \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}}_{\hat{\sigma}_v^{(1)}} \begin{pmatrix} x \\ y \end{pmatrix}.$$

Since $2\cos(2\pi/3) = 2\cos(4\pi/3) = -1$, this confirms that the character for $2\hat{C}_3$ is equal to -1. The character for $\hat{E}$ is equal to 2 because this is a matrix in two dimensional vector space. The character for $\hat{\sigma}_v$ is equal to zero as can be seen from its matrix representation. Note that the number of classes is equal to the number

of irreducible representations. In addition, the order of C_{3v} group, $Q = 6$, is also equal to $1^2 + 1^2 + 2^2$, which is the sum of squares of the dimensions of all the irreducible representations. In fact, these relationships are true for C_{2v} and for all the point groups.

Relationships Between the Order, the Number of Classes, and the Number of Irreducible Representations

- The number of classes is equal to the number of irreducible representations.
- The order of a group Q is equal to the sum of squared dimensions of all irreducible representations.

The importance of irreducible representations is that they can be regarded as an orthogonal basis in defining any representation. In other words, given a representation in a certain basis, the following decomposition always exists uniquely:

$$\Gamma = \sum_{k=1}^{P} a_k \Gamma'_k, \tag{9.87}$$

where a_k is a nonnegative integer, Γ'_k is an irreducible representation Γ_k embedded in the full dimension of Γ so that all other matrix elements except for the block of Γ_k are zero, and P is the total number of irreducible representations in the group. Thus, both Γ_k and Γ'_k have the same trace.

An important theorem concerning the characters of irreducible representations is their orthogonality as stated below.

Orthogonality Theorem

Given two different irreducible representations Γ_j and Γ_k, the following relation holds:

$$\frac{1}{Q}\sum_{i=1}^{Q} \chi_j[\hat{S}_i]^* \chi_k[\hat{S}_i] = \delta_{jk}, \tag{9.88}$$

where $\chi_j[\hat{S}_i]$ is the character of the irreducible representation Γ_j for the symmetry operation $\hat{S}_i$. This is a special case of the most general great orthogonality theorem given by Theorem 9.6, provided in the Appendix of this chapter, as described below.

(continued)

For the present case, the group elements G's in Eq. (9.135) of the Appendix are symmetry operators, $\hat{S}_j$'s. Since the trace is given by

$$\chi_j[\hat{S}_i] = \sum_{m=1}^{l_j} [\mathbf{\Gamma}^{(j)}(\hat{S}_i)]_{mm}, \tag{9.89}$$

we find that

$$\begin{aligned}\sum_{i=1}^{Q} \chi_j[\hat{S}_i]^* \chi_k[\hat{S}_i] &= \sum_{m=1}^{l_j} \sum_{n=1}^{l_k} \sum_{i=1}^{Q} [\mathbf{\Gamma}^{(j)}(\hat{S}_i)]^*_{mm} [\mathbf{\Gamma}^{(k)}(\hat{S}_i)]_{nn} \\ &= \sum_{m=1}^{l_j} \sum_{n=1}^{l_k} \frac{Q}{l_j} \delta_{jk} \delta_{mn} = Q \delta_{jk}.\end{aligned} \tag{9.90}$$

Dividing the above expression with Q, we obtain Eq. (9.88).

Given the decomposition of a (reducible) representation Γ according to Eq. (9.87), the same relationship should hold for the character of any symmetry operation as follows:

$$\chi_\Gamma[\hat{S}_i] = \sum_{k=1}^{P} a_k \chi_k[\hat{S}_i], \tag{9.91}$$

where $\chi_\Gamma[\hat{S}_i]$ is the character of the reducible representation Γ for the symmetry operation $\hat{S}_i$. Multiplying the above equation with $\chi_l[\hat{S}_j]^*$ and summing over all the symmetry operations of the group, $\hat{S}_i$, and dividing with Q, the order of the group, we obtain

$$\frac{1}{Q} \sum_{i=1}^{Q} \sum_{k=1}^{P} \chi_j[\hat{S}_i]^* a_k \chi_k[\hat{S}_i] = \sum_{k=1}^{P} a_k \delta_{jk} = a_j, \tag{9.92}$$

where Eq. (9.88) has been used. The above expression confirms that each coefficient a_k in the expansion, Eq. (9.87), can be obtained only from the information on the characters for all symmetry operations

9.4.5 Application for Symmetry Adapted LCAO-MO

Let us consider an example of water molecule, which belongs to the C_{2v} group, and assume LCAO-MOs consisting of six atomic orbitals,

$$|\psi_{MO}\rangle = C_{sA}|S_A\rangle + C_{sB}|S_B\rangle + c_{sC}|S_C\rangle + c_{px}|p_x\rangle + c_{py}|p_y\rangle + c_{pz}|p_z\rangle, \tag{9.93}$$

where $|S_A\rangle$ and $|S_B\rangle$ are $1s$ orbital states of two hydrogen atoms, respectively denoted as A and B, $|S_C\rangle$ is the $2s$ orbital state of the central oxygen atom, $|p_x\rangle$, $|p_y\rangle$, and $|p_z\rangle$ are p_x, p_y, p_z orbital states of the oxygen atom. The molecule is assumed to be in the yz-plane. Thus, xy-plane bisects the two hydrogen atoms. All the representations of the symmetry operators in this basis can be identified by finding out the outcomes of their actions on the vectors of six orbital states as described below. First, the representation of $\hat{C}_2$ operation is obtained by

$$\hat{C}_2 \begin{pmatrix} S_A \\ S_B \\ S_C \\ p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} S_B \\ S_A \\ S_C \\ -p_x \\ -p_y \\ p_z \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} S_A \\ S_B \\ S_C \\ p_x \\ p_y \\ p_z \end{pmatrix}, \tag{9.94}$$

where for convenience we have omitted the ket symbols for the atomic orbital states. The actions of other operators in the C_{2v} group can be identified similarly. Thus,

$$\hat{\sigma}_v \begin{pmatrix} S_A \\ S_B \\ S_C \\ p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} S_B \\ S_A \\ S_C \\ p_x \\ -p_y \\ p_z \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} S_A \\ S_B \\ S_C \\ p_x \\ p_y \\ p_z \end{pmatrix}, \tag{9.95}$$

$$\hat{\sigma}_v' \begin{pmatrix} S_A \\ S_B \\ S_C \\ p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} S_A \\ S_B \\ S_C \\ -p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} S_A \\ S_B \\ S_C \\ p_x \\ p_y \\ p_z \end{pmatrix}. \tag{9.96}$$

Matrices shown above are matrix representations of the symmetry operations in the basis of the six atomic orbitals. Thus, including the identity operation, which is represented by a six dimensional unit matrix, one can calculate the characters for all the symmetry operations as listed in the table below.

C_{2v}	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}'_v(yz)$
Γ	6	0	2	4

Using the orthogonality theorem, we can identify the coefficients for irreducible representations for the above reducible representation as follows:

$$A_1 : \frac{1}{4}(1 \cdot 6 + 1 \cdot 0 + 1 \cdot 2 + 1 \cdot 4) = 3$$

$$A_2 : \frac{1}{4}(1 \cdot 6 + 1 \cdot 0 + (-1) \cdot 2 + (-1) \cdot 4) = 0$$

$$B_1 : \frac{1}{4}(1 \cdot 6 + (-1) \cdot 0 + 1 \cdot 2 + (-1) \cdot 4) = 1$$

$$A_2 : \frac{1}{4}(1 \cdot 6 + (-1) \cdot 0 + (-1) \cdot 2 + 1 \cdot 4) = 2$$

Therefore, we find that

$$\Gamma = 3A_1 + B_1 + 2B_2. \tag{9.97}$$

This implies that the MOs that are simultaneous eigenstates of the symmetry operations of the C_{2v} group, which can be constructed out of the six atomic orbitals are three MOs with the symmetry of A_1, one MO with the symmetry of B_1, and two MOs with the symmetry of B_2. Due to the simplicity of water molecule, these MOs can be identified easily by inspection.

Indeed, it is clear that the three MOs with A_1 symmetry correspond to $(|S_A\rangle + |S_B\rangle)/\sqrt{2}$, $|S_C\rangle$, and $|p_z\rangle$. The MO with B_1 symmetry is the p_x orbital of oxygen and thus corresponds to $|p_x\rangle$. Two MOs with B_2 symmetry are $(|S_A\rangle - |S_B\rangle)/\sqrt{2}$ and $|p_z\rangle$. Note that these are not yet bonding or anti-bonding orbitals, but can be used to construct them easily because only MOs belonging to the same irreducible representations can be combined together. This implies that at least three bonding/anti-bonding MOs can be constructed from the three MOs with A_1 symmetry and that bonding and anti-bonding MOs can be constructed from the two MOs with B_2 symmetry. On the other hand, the single orbital with B_1 symmetry, $|p_x\rangle$, is expected to remain as nonbonding. Figure 9.7 shows four MOs obtained from a HF calculation, and indicates that the simple analysis based on the group theory can indeed explain qualitative patterns of the lowest unoccupied molecular orbital (LUMO), the highest occupied molecular orbital (HOMO) and HOMO-1.

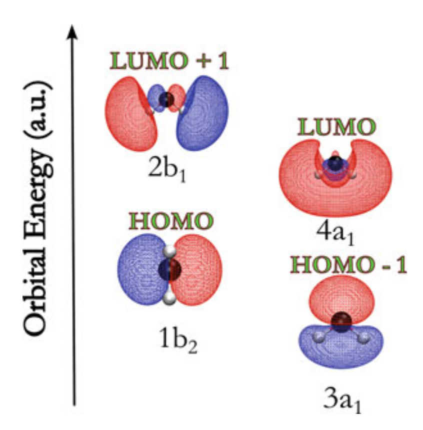


Fig. 9.7 Four MOs of a water molecule, highest occupied MO (HOMO), lowest unoccupied MO (LUMO), HOMO-1, and LUMO+1 obtained from a Hartree-Fock calculation. Their symmetry properties are also shown

9.5 Spectroscopy of Polyatomic Molecules

Within the BO approximation, the eigenstates of the molecular Hamiltonian can be decoupled to electronic and nuclear parts as described in Sect. 9.1. Given that the potential energy surfaces $V_{BO,a}(\mathbf{R})$ can be determined by solving the electronic Schrödinger equation, Eq. (9.9), for all possible values of the nuclear coordinates,[7] one can then obtain the Schrödinger equation for the nuclear degrees of freedom, Eq. (9.19). This Schrödinger equation can again be decomposed into translation, rotation, and vibrational components. In the absence of external potential, the translational components can be ignored.

9.5.1 Infrared and Raman Spectroscopy

As in the case of diatomic molecules, the selection rules for the IR and Raman spectroscopy are the same. In other words, $\Delta v = \pm 1$ in both cases. However, for general polyatomic molecules with many vibrational normal modes, determining which modes are IR and Raman active is not a simple task. The group theory and character table for each group is very helpful in this respect.

Given a molecule, we can identify a point group with the maximum number of symmetry operations with respect to which the molecule remains invariant. Then, we can determine the characters for the reducible representation of all the

[7] While this is possible in principle, it is almost impossible in practice for most polyatomic molecules. Thus, only partial information around local minima around the minimum of each electronic state is typically available.

coordinates for operations in the group. Application of the orthogonality theorem then allows determining the linear combination of irreducible representations. Once all the translational and rotational modes are subtracted, the IR active modes correspond to those that behave like x, y, and z. The Raman active modes correspond to those that behave like quadratic functions of the coordinates.

Let us once again consider the water molecule as an example. For this, consider the representation of the symmetry operations in the nine dimensional cartesian coordinates consisting of x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, and z_3, where the subscript 1 denotes the coordinates of the oxygen and 2 and 3 denote the coordinates of two hydrogen atoms. In this basis, the character of the identity operator $\chi(\hat{E}) = 9$. The operation of $\hat{C}_2$ can be represented according to the following relation:

$$\hat{\mathrm{C}}_2 \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix} = \begin{pmatrix} -x_1 \\ -y_1 \\ z_1 \\ -x_3 \\ -y_3 \\ z_3 \\ -x_2 \\ -y_2 \\ z_2 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix}, \tag{9.98}$$

for which $\chi(\hat{\mathrm{C}}_2) = -1$. The operation of $\hat{\sigma}_v$ can be represented according to the following relation:

$$\hat{\sigma}_v \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix} = \begin{pmatrix} x_1 \\ -y_1 \\ z_1 \\ x_3 \\ -y_3 \\ z_3 \\ x_2 \\ -y_2 \\ z_2 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix}, \tag{9.99}$$

for which $\chi(\sigma_v) = 1$. Finally, the operation of $\hat{\sigma}_v'$ can be represented according to the following relation:

$$\hat{\sigma}_v' \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix} = \begin{pmatrix} -x_1 \\ y_1 \\ z_1 \\ -x_2 \\ y_2 \\ z_2 \\ -x_3 \\ y_3 \\ z_3 \end{pmatrix} = \begin{pmatrix} -1\,0\,0 & 0\,0\,0 & 0\,0\,0 \\ 0\,1\,0 & 0\,0\,0 & 0\,0\,0 \\ 0\,0\,1 & 0\,0\,0 & 0\,0\,0 \\ 0\,0\,0 & -1\,0\,0 & 0\,0\,0 \\ 0\,0\,0 & 0\,1\,0 & 0\,0\,0 \\ 0\,0\,0 & 0\,0\,1 & 0\,0\,0 \\ 0\,0\,0 & 0\,0\,0 & -1\,0\,0 \\ 0\,0\,0 & 0\,0\,0 & 0\,1\,0 \\ 0\,0\,0 & 0\,0\,0 & 0\,0\,1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix}, \tag{9.100}$$

for which $\chi(\hat{\sigma}_v') = 3$. Summing up all these results, we obtain all the characters for the reducible representation as listed in the table below.

C_{2v}	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}_v'(yz)$
Γ	9	−1	1	3

Application of the orthogonality theorem then leads to

$$A_1 : \frac{1}{4}(9 - 1 + 1 + 3) = 3$$

$$A_2 : \frac{1}{4}(9 - 1 - 1 - 3) = 1$$

$$B_1 : \frac{1}{4}(9 + 1 + 1 - 3) = 2$$

$$B_2 : \frac{1}{4}(9 + 1 - 1 + 3) = 3$$

Therefore, we find that

$$\Gamma = 3A_1 + A_2 + 2B_1 + 3B_2. \tag{9.101}$$

Out of the above linear combinations, the translational motion of the molecule corresponds to $\Gamma_{tr} = A_1 + B_1 + B_2$ and the rotational motion corresponds to $\Gamma_{rot} = A_2 + B_1 + B_2$ according to the character table of C_{2v}. Thus, subtracting these from Γ given above, we obtain the following decomposition of the vibrational reducible representation:

$$\Gamma_{vib} = 2A_1 + B_2. \tag{9.102}$$

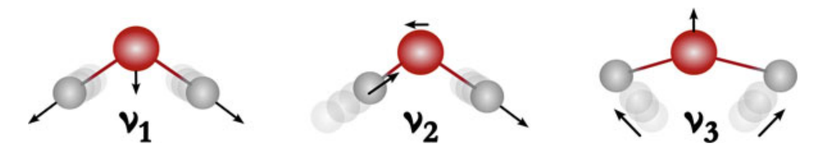


Fig. 9.8 Three vibrational modes of a water molecule

Thus, there are two vibrational modes with A_1 symmetry, which correspond to symmetric stretching and bending, and one vibrational mode with B_2 symmetry, which is asymmetric stretching (see Fig. 9.8). Both of these symmetries contain those that are linear and quadratic in the cartesian coordinates. Therefore, they are both IR and Raman active.

9.5.2 Electronic Spectroscopy

In general, the electronic spectroscopy involves transition between electronic states due to the interaction between the electric field part of the radiation and the following full dipole operator involving electrons,

$$\hat{\boldsymbol{D}}_T(\hat{\mathbf{r}}, \hat{\mathbf{R}}) = e \left\{ \sum_{c=1}^{N_u} Z_c \hat{\mathbf{R}}_c - \sum_{\nu=1}^{N_e} \hat{\mathbf{r}}_\nu \right\}, \tag{9.103}$$

where the Z_c and $\hat{\mathbf{R}}_c$ are nuclear charges and position operators and the $\hat{\mathbf{r}}_\nu$ are the position operators of the electron ν. Thus, in general, the electronic transition involving one photon is allowed as long as the following transition dipole vector is nonzero.

$$\boldsymbol{D}_{if}^{tr} = \langle \Psi_f | \hat{D}_T(\hat{\mathbf{r}}, \hat{\mathbf{R}}) | \Psi_i \rangle, \tag{9.104}$$

where $|\Psi_i\rangle$ and $|\Psi_f\rangle$ refer to initial and final molecular states including both electronic and nuclear degrees of freedom. Let us assume that the initial and final states can be approximated as the product of electronic states and nuclear wave function in respective BO surfaces as follows:

$$\begin{aligned} |\Psi_i\rangle &= \int d\mathbf{r} \int d\mathbf{R}\, |\mathbf{r}, \mathbf{R}\rangle\langle \mathbf{r}, \mathbf{R}|\Psi_i\rangle \\ &= \int d\mathbf{r} \int d\mathbf{R}\, |\mathbf{r}, \mathbf{R}\rangle \psi_{nu_i}(\mathbf{R}) \psi_{e_i}(\mathbf{r}; \mathbf{R}), \end{aligned} \tag{9.105}$$

$$
\begin{aligned}
|\Psi_f\rangle &= \int d\mathbf{r} \int d\mathbf{R}\, |\mathbf{r}, \mathbf{R}\rangle\langle\mathbf{r}, \mathbf{R}|\Psi_f\rangle \\
&= \int d\mathbf{r} \int d\mathbf{R}\, |\mathbf{r}, \mathbf{R}\rangle \psi_{nu_f}(\mathbf{R})\psi_{e_f}(\mathbf{r}; \mathbf{R}).
\end{aligned} \tag{9.106}
$$

Then,

$$
\boldsymbol{D}_{if}^{tr} = \int d\mathbf{R}\, \psi_{nu_f}^*(\mathbf{R})\psi_{nu_i}(\mathbf{R}) \int d\mathbf{r}\, \psi_{e_f}^*(\mathbf{r}; \mathbf{R})\hat{\boldsymbol{D}}_T(\mathbf{r}, \mathbf{R})\psi_{e_i}(\mathbf{r}; \mathbf{R}). \tag{9.107}
$$

In many electronic transitions, it turns out that the integration of the dipole operator with respect to the electronic degrees of freedom can be approximated in terms of the following electronic transition dipole vector calculated for a reference nuclear coordinate:

$$
\begin{aligned}
\boldsymbol{D}_{if}^{e}(\mathbf{R}_0) &= \int d\mathbf{r}\, \psi_{e_f}^*(\mathbf{r}; \mathbf{R}_0)\hat{D}_T(\mathbf{r}, \mathbf{R}_0)\psi_{e_i}(\mathbf{r}; \mathbf{R}_0) \\
&= -e \int d\mathbf{r}\, \psi_{e_f}^*(\mathbf{r}; \mathbf{R}_0) \left(\sum_{\nu} \mathbf{r}_{\nu} \right) \psi_{e_i}(\mathbf{r}; \mathbf{R}_0),
\end{aligned} \tag{9.108}
$$

where $\mathbf{R}_0$ is the reference nuclear coordinates that are typically assumed to be the coordinates for the minimum of the initial electronic state and the second equality results from the fact that the two electronic states determined for the nuclear coordinate $\mathbf{R}_0$ are orthogonal to each other. This is so called Franck-Condon approximation, and the resulting approximation for the total transition dipole vector is as follows:

$$
\boldsymbol{D}_{if}^{tr} \approx \boldsymbol{D}_{if}^{e} \int d\mathbf{R}\, \psi_{nu_f}^*(\mathbf{R})\psi_{nu_i}(\mathbf{R}), \tag{9.109}
$$

where the overlap integration of the nuclear wavefunction is nonzero in general because they are defined with respect different structures and is known as the Franck-Condon factor.

For electronic absorption spectroscopy, the initial state is the ground electronic state (labeled as X) and the transition occurs to an electronic state with the same spin multiplicity as the ground state (labeled as A, B, C, etc) and with nonzero value of the electronic transition dipole vector given by Eq. (9.108). For small molecules where all the vibrational frequencies are much larger than thermal energy, $\psi_{nu_i}(\mathbf{R})$ can be approximated well by the product of ground state vibrational wave functions of all the vibrational normal modes.

For the case of radiative electronic emission spectroscopy, normally called fluorescence, the initial state is one of the excited electronic states (A, B, C, etc), which has the same spin multiplicity as the ground electronic state (X). In this case as well, if the vibrational frequencies in the excited electronic state are much larger

than the thermal energy, the initial nuclear wave function can be approximated well by the product of ground vibrational state wave functions of all normal modes in the excited electronic state potential energy surface.

Although fluorescence is the dominant mechanism of transitions of excited electronic state, there are other non-radiative transitions that can occur as well. If the non-radiative transition is between excited states of the same spin multiplicity, it is called internal conversion. If the transition occurs to states with different spin multiplicity (labeled as a, b, c, etc), it is called intersystem crossing. The mechanism of this intersystem crossing is spin-orbit coupling. Radiative transition from excited states with different spin multiplicity to the ground electronic state can occur although it is dipole forbidden. This process is called phosphorescence and typically takes microseconds and beyond.

9.6 Summary and Questions

Within the BO approximation, quantum states of polyatomic molecules can be treated in two stages. First, ignoring the kinetic energy of nuclei, the Schrödinger equation for electrons for fixed nuclei can be solved. Then, energies obtained from these calculations for all possible nuclear coordinates (in principle) can be incorporated into the potential energy for nuclei so as to describe the vibrational states of molecules. Although conceptually straightforward, even solving the equations for electrons alone involves challenging numerical issues, for which various approximation methods have been developed.

One of the simplest approximations that can be used for obtaining electronic states in polyatomic molecules is to use LCAO-MOs and assume that electrons can be filled in independent of each other while satisfying the Pauli principle. This simple treatment leads to qualitatively correct description of small or simple molecules, helping to understand important molecular quantum mechanical details without going through numerical calculations. Representative examples are diatomic molecules of the second row, for which Table 9.1 sums up major results. Verification or further correction of the simple MO description can be made through photoelectron spectroscopy in combination with Koopmans' theorem given by Eq. (9.53).

Another important application of the LCAO-MO approximation is approximating π-orbital energies of conjugated hydrocarbons, for which additional Hückel approximation can also be made. This simple model has helped to understand the types of conjugated hydrocarbons that can be stabilized and also contributed to developing semi-empirical methods during early stages of electronic structure calculation method development.

For the understanding and description of both electronic and vibrational states of polyatomic molecules, group theory has also provided important conceptual framework for understanding the symmetry of states and relevant selection rules. The success of the group theory relies on the fact that a set of symmetry

operations that leave a certain molecule invariant can form a mathematical group. The properties of the group then can be employed to classify electronic and vibrational states of molecules. The most important theorem in such application is the orthogonality theorem, based on which efficient ways to construct MOs and to identify types of vibrational modes have been developed. In particular, for the vibrational spectroscopy, identification of irreducible representations and referral of the character table make it possible to determine IR and Raman active vibrational normal modes of a molecule.

Questions

- What are neglected in the BO approximation and when do they become significant?
- Is it possible to use the LCAO-MO approximation to describe formation and breaking of chemical bonds?
- The component of the total orbital angular momentum along the internuclear axis in a diatomic molecule is conserved. What is the reason for this?
- The relative order of bonding σ and π orbitals for O_2 and F_2 are different from other diatomic molecules with smaller atomic numbers in the second row. What is the reason for this?
- What are additional assumptions involved in the Hückel approximation in addition to the LCAO-MO approximation?
- Koopmans' theorem is known to be fairly accurate despite its simple expression and even though it does not account for electron correlation effects. What is the implication of this success?
- When does a molecule have vibrational modes that are both IR and Raman active?
- If a molecule belongs to a certain point group, all the symmetry operations constituting the point group commute with the Hamiltonian of the molecule. What is the reason for this?
- What is the difference between reducible and irreducible representations in the group theory?

Appendix: Important Theorems and Proofs in the Group Theory

This appendix provides a complete set of theorems and proofs for obtaining the orthogonality theorem, Eq. (9.88). The theorems and proofs presented here are based on those presented by Tinkham [10], with some alternation in notations and additional clarifications.

Theorem 9.1 *Rearrangement theorem: For any group $\mathcal{G}$, the multiplication of any element of the group with all the elements of the group produce a complete set containing all the elements, where each element of the group appears only once.*

Proof Consider a set $\mathcal{S}$ consisting of all the group elements multiplied with X, which is also an element of the group. For convenience, assume that each element is multiplied with X on the right.

Let us choose an arbitrary element of the group, say A. Then, the group $\mathcal{G}$ should contain $B = A \circ X^{-1}$ as its element because there should be an inverse of X in the group and the group is closed with respect to multiplication. Since $B \circ X = A$, A should appear at least once in the set $\mathcal{S}$. Thus, (i) any group element of $\mathcal{G}$ should exist in the set $\mathcal{S}$.

Since $\mathcal{S}$ and the original set of $\mathcal{G}$ have the same number of elements, each element should appear only once in the set of products. Otherwise, there should be an element that cannot appear, which is contradictory with the statement (i). This completes the proof for the case where the elements are multiplied with X on the right. Similar proof is possible for the case where X is multiplied on the left by considering $X^{-1} \circ A$. □

As a result of the above theorem, the following identity holds for any sum over all the elements of the group:

$$\sum_k F(A_k) = \sum_k F(A_k \circ X) = \sum_k F(X \circ A_k), \tag{9.110}$$

where F is an arbitrary function, A_k's for all k constitute the complete set of element of the group, and X is an arbitrary element of the group.

Theorem 9.2 *Any matrix representation of a group is equivalent to a representation by a unitary matrix as long as determinants of all the matrices are nonzero.*

Proof Let us denote the matrix representing the ith element of the group as $\mathbf{A}_i$, where $i = 1, \cdots, Q$. Then, one can always construct the following Hermitian matrix:

$$\mathbf{H} = \sum_{i=1}^{Q} \mathbf{A}_i \mathbf{A}_i^\dagger, \tag{9.111}$$

where $\mathbf{A}_i^\dagger$ is the Hermitian conjugate of $\mathbf{A}_i$. Therefore, $\mathbf{H}$ can be diagonalized to $\mathbf{H}'$ by a unitary matrix $\mathbf{U}$ as follows:

$$\mathbf{H}' = \mathbf{U}^\dagger \mathbf{H} \mathbf{U} = \sum_{i=1}^{Q} \mathbf{U}^\dagger \mathbf{A}_i \mathbf{A}_i^\dagger \mathbf{U} = \sum_{i=1}^{Q} \mathbf{A}_i' \mathbf{A}_i'^\dagger, \tag{9.112}$$

where $\mathbf{A}'_i = \mathbf{U}^\dagger \mathbf{A}_i \mathbf{U}$. Note that

$$[\mathbf{H}']_{jj} = \sum_{i=1}^{Q} \sum_{k} [\mathbf{A}'_i]_{jk} [\mathbf{A}'^{\dagger}_i]_{kj} = \sum_{i=1}^{Q} \sum_{k} \left| [\mathbf{A}'_i]_{jk} \right|^2 . \tag{9.113}$$

Therefore, all the diagonal elements of $\mathbf{H}'$ are real and positive, and we can define $\mathbf{H}'^{1/2}$ and $\mathbf{H}'^{-1/2}$. Therefore, Eq. (9.112) can also be expressed as

$$\mathbf{I} = \mathbf{H}'^{-1/2} \left(\sum_{i=1}^{Q} \mathbf{A}'_i \mathbf{A}'^{\dagger}_i \right) \mathbf{H}'^{-1/2}, \tag{9.114}$$

where $\mathbf{I}$ is the identity matrix. Now, let us consider a new transformed matrices $\mathbf{A}''_j = \mathbf{H}'^{-1/2} \mathbf{A}'_j \mathbf{H}'^{1/2}$ for all $j = 1, \cdots, Q$. Then, these can be shown to be unitary as follows:

$$\begin{aligned}
\mathbf{A}''_j \mathbf{A}''^{\dagger}_j &= \mathbf{H}'^{-1/2} \mathbf{A}'_j \mathbf{H}'^{1/2} \mathbf{I} \mathbf{H}'^{1/2} \mathbf{A}'^{\dagger}_j \mathbf{H}'^{-1/2} \\
&= \mathbf{H}'^{-1/2} \mathbf{A}'_j \mathbf{H}'^{1/2} \mathbf{H}'^{-1/2} \left(\sum_{i=1}^{Q} \mathbf{A}'_i \mathbf{A}'^{\dagger}_i \right) \mathbf{H}'^{-1/2} \mathbf{H}'^{1/2} \mathbf{A}'^{\dagger}_j \mathbf{H}'^{-1/2} \\
&= \mathbf{H}'^{-1/2} \left(\sum_{i=1}^{Q} \mathbf{A}'_j \mathbf{A}'_i \mathbf{A}'^{\dagger}_i \mathbf{A}'^{\dagger}_j \right) \mathbf{H}'^{-1/2} \\
&= \mathbf{H}'^{-1/2} \left(\sum_{k=1}^{Q} \mathbf{A}'_k \mathbf{A}'^{\dagger}_k \right) \mathbf{H}'^{-1/2} = \mathbf{I},
\end{aligned} \tag{9.115}$$

where in the second and last equality, Eq. (9.114) has been used and Eq. (9.110) in matrix representation has been used for $\mathbf{A}'_k = \mathbf{A}'_j \mathbf{A}'_i$. Now, each $\mathbf{A}''_j$ is related to $\mathbf{A}_j$ as follows:

$$\begin{aligned}
\mathbf{A}''_j &= \mathbf{H}'^{-1/2} \mathbf{U}^\dagger \mathbf{A}_j \mathbf{U} \mathbf{H}'^{1/2} = \mathbf{H}'^{-1/2} \mathbf{U}^{-1} \mathbf{A}_j \mathbf{U} \mathbf{H}'^{1/2} \\
&= \left(\mathbf{U} \mathbf{H}'^{1/2} \right)^{-1} \mathbf{A}_j \mathbf{U} \mathbf{H}'^{1/2}.
\end{aligned} \tag{9.116}$$

Thus, $\mathbf{A}''_j$ is related to $\mathbf{A}_j$ by a similarity transformation. This completes the proof. □

Theorem 9.3 *Any Hermitian matrix commuting with all matrices of an irreducible representation must be a constant matrix.*

Proof Let us denote the Hermitian matrix that commutes with all matrices of a representation of a group as $\mathbf{H}$. This implies that

$$\mathbf{A}_i\mathbf{H} = \mathbf{H}\mathbf{A}_i, \text{ for } i = 1, \cdots, Q \tag{9.117}$$

Since $\mathbf{H}$ is Hermitian, there should be a unitary matrix $\mathbf{U}$ such that $\mathbf{H}' = \mathbf{U}^\dagger\mathbf{H}\mathbf{U}$ is diagonal. Then, applying $\mathbf{U}^\dagger$ and $\mathbf{U}$ on the left and right side of the above equation, we obtain

$$\mathbf{A}_i'\mathbf{H}' = \mathbf{H}'\mathbf{A}_i', \tag{9.118}$$

where $\mathbf{A}_i' = \mathbf{U}^\dagger\mathbf{A}\mathbf{U} = \mathbf{U}^{-1}\mathbf{A}\mathbf{U}$. Taking the matrix element of the above relation and using the fact that the $\mathbf{H}'$ has only diagonal elements, we obtain

$$[\mathbf{A}_i']_{nm}[\mathbf{H}']_{mm} = [\mathbf{H}']_{nn}[\mathbf{A}_i']_{nm}, \tag{9.119}$$

which means that

$$[\mathbf{A}_i']_{nm}\left([\mathbf{H}']_{mm} - [\mathbf{H}']_{nn}\right) = 0. \tag{9.120}$$

If all the diagonal elements of $\mathbf{H}$ are the same, the above identity is satisfied. On the other hand, if $[\mathbf{H}']_{mm} - [\mathbf{H}']_{nn} \neq 0$ for some $n \neq m$, the above identity means that $[\mathbf{A}_i']_{nm} = 0$ for all i. This implies that the unitary transformation of $\mathbf{A}_i$'s to $\mathbf{A}_i'$'s resulted in smaller blocks. However, this contradicts the assumption that $\mathbf{A}_i$'s are irreducible, Therefore, all the diagonal matrix elements of $\mathbf{H}'$ should be the same. Thus, $\mathbf{H}' = c\mathbf{I}$, where c is an arbitrary constant, and $\mathbf{H} = c\mathbf{U}\mathbf{I}\mathbf{U}^\dagger = c\mathbf{I}$. □

Theorem 9.4 *Schur's Lemma: Any matrix commuting with all matrices of an irreducible representation must be a constant matrix.*

Proof Let us denote the matrix that commutes with all matrices of a representation of a group as $\mathbf{M}$. This implies that

$$\mathbf{A}_i\mathbf{M} = \mathbf{M}\mathbf{A}_i, \text{ for } i = 1, \cdots, Q \tag{9.121}$$

Taking the Hermitian conjugate of the above relationship, we obtain

$$\mathbf{M}^\dagger\mathbf{A}_i^\dagger = \mathbf{A}_i^\dagger\mathbf{M}^\dagger. \tag{9.122}$$

Then, by multiply $\mathbf{A}_i$ and $\mathbf{A}_i$ on the left and right side of the above expression, we obtain

$$\mathbf{A}_i\mathbf{M}^\dagger\mathbf{A}_i^\dagger\mathbf{A}_i = \mathbf{A}_i\mathbf{A}_i^\dagger\mathbf{M}^\dagger\mathbf{A}_i. \tag{9.123}$$

According to Theorem 9.2, we can always find out a representation where all $\mathbf{A}$'s are unitary by similarity transformation. Thus, let us define such a transformation

matrix as $\mathbf{S}$, which has inverse, and let $\mathbf{A}_i' = \mathbf{S}^{-1}\mathbf{A}_i\mathbf{S}$. Then, multiplying $\mathbf{S}^{-1}$ and $\mathbf{S}$ on the left and right hand side of the above expression, and inserting $\mathbf{1} = \mathbf{S}^{-1}\mathbf{S}$ between every operator, we obtain

$$\mathbf{A}_i'\mathbf{S}^{-1}\mathbf{M}^\dagger\mathbf{S}\mathbf{A}_i'^\dagger\mathbf{A}_i' = \mathbf{A}_i'\mathbf{A}_i'^\dagger\mathbf{S}^{-1}\mathbf{M}^\dagger\mathbf{S}\mathbf{A}_i'. \tag{9.124}$$

Since $\mathbf{A}_i'$'s are unitary, the above relation implies that

$$\mathbf{A}_i'\mathbf{M}'^\dagger = \mathbf{M}'^\dagger\mathbf{A}_i', \tag{9.125}$$

where $\mathbf{M}' = \mathbf{S}^{-1}\mathbf{M}^\dagger\mathbf{S}$. On the other hand, applying the same similarity transformation to Eq. (9.121), we obtain

$$\mathbf{A}_i'\mathbf{M}' = \mathbf{M}'\mathbf{A}_i', \tag{9.126}$$

Now, let us defined $\mathbf{H}_1 = \mathbf{M}' + \mathbf{M}'^\dagger$ and $\mathbf{H}_2 = i(\mathbf{M}' - \mathbf{M}'^\dagger)$. Then, employing Eqs. (9.125) and (9.126), we find that

$$\mathbf{A}_i'\mathbf{H}_1 = \mathbf{H}_1\mathbf{A}_i', \tag{9.127}$$

$$\mathbf{A}_i'\mathbf{H}_2 = \mathbf{H}_2\mathbf{A}_i', \tag{9.128}$$

for all $i = 1, \cdots, Q$. According to Theorem 9.3, $\mathbf{H}_1$ and $\mathbf{H}_2$ are constant matrices. Therefore, $\mathbf{M}'$ is constant matrix and $\mathbf{M} = \mathbf{S}\mathbf{M}'\mathbf{S}^{-1}$ is also a constant matrix. □

Theorem 9.5 *There are two irreducible matrix representations of the same group, $\mathbf{\Gamma}^{(1)}(A_i)$ and $\mathbf{\Gamma}^{(2)}(A_i)$, each with dimensionality l_1 and l_2. Let us assume that a rectangular matrix $\mathbf{M}$ exists such that*

$$\mathbf{M}\mathbf{\Gamma}^{(1)}(A_i) = \mathbf{\Gamma}^{(2)}(A_i)\mathbf{M}, \tag{9.129}$$

for all $i = 1, \cdots, Q$. Then, the following is true. For $l_1 \neq l_2$, $\mathbf{M} = 0$. For $l_1 = l_2$, either $\mathbf{M} = 0$ or the determinant of $\mathbf{M}$ is nonzero, for which the two irreducible representations are equivalent.

Proof Assume that all the irreducible matrices are unitary as well. If not, they can be transformed to unitary matrices according to Theorem 9.2. Then, taking the Hermitian conjugate of Eq. (9.129) and using the fact that the matrix representations are unitary,

$$\mathbf{\Gamma}^{(1)}(A_i^{-1})\mathbf{M}^\dagger = \mathbf{\Gamma}^{(1)}(A_i)^\dagger\mathbf{M}^\dagger = \mathbf{M}^\dagger\mathbf{\Gamma}^{(2)}(A_i)^\dagger = \mathbf{M}^\dagger\mathbf{\Gamma}^{(2)}(A_i^{-1}). \tag{9.130}$$

Multiplying the above expression with $\mathbf{M}$ on the lefthand side and using the fact that $\mathbf{M}\boldsymbol{\Gamma}^{(1)}(A_i^{-1}) = \boldsymbol{\Gamma}^{(2)}(A_i^{-1})\mathbf{M}$, which is a specific case of Eq. (9.129) for A_i^{-1}, we obtain the following expression:

$$\mathbf{M}\boldsymbol{\Gamma}^{(1)}(A_i^{-1})\mathbf{M}^\dagger = \boldsymbol{\Gamma}^{(2)}(A_i^{-1})\mathbf{M}\mathbf{M}^\dagger = \mathbf{M}\mathbf{M}^\dagger\boldsymbol{\Gamma}^{(2)}(A_i^{-1}). \tag{9.131}$$

Since the above relation holds for any A_i^{-1} in the group, according to Theorem 9.4, the above relation implies that

$$\mathbf{M}\mathbf{M}^\dagger = c\mathbf{I}, \tag{9.132}$$

where $\mathbf{I}$ is the identity matrix of dimension l_1.

If $l_1 = l_2$, Eq. (9.134) implies that the absolute square of the determinant of $\mathbf{M}$ is equal to c^{l_1}. For the case where $c \neq 0$, this implies that the determinant of $\mathbf{M}$ is nonzero. For the case where $c = 0$, considering the diagonal elements of Eq. (9.134), we find that

$$\sum_n [\mathbf{M}]_{mn}[\mathbf{M}^\dagger]_{nm} = \sum_n |[\mathbf{M}]_{mn}|^2 = 0. \tag{9.133}$$

The above identity holds true only when all the matrix elements are zero.

If $l_1 < l_2$, we can create a square matrix of dimension l_2 by adding $(l_2 - l_1)$ columns of zeros to $\mathbf{M}$. Then, $\mathbf{N}\mathbf{N}^\dagger = \mathbf{M}\mathbf{M}^\dagger$. Therefore,

$$\mathbf{N}\mathbf{N}^\dagger = c\mathbf{I}. \tag{9.134}$$

Since the determinant of $\mathbf{N}$ is zero, the above identity implies that $c = 0$. Then, the proof for the case of $l_1 = l_2$ above can again be applied to show that $\mathbf{N} = 0$.

If $l_1 > l_2$, similar proof is possible by constructing a square matrix of dimension l_1 by inserting $l_1 - l_2$ rows of zeros in $\mathbf{M}$. □

Theorem 9.6 *The great orthogonality theorem: For all possible irreducible and unitary representations of a group,*

$$\sum_G [\boldsymbol{\Gamma}^{(j)}(G)]^*_{mm'}[\boldsymbol{\Gamma}^{(k)}(G)]_{nn'} = \frac{Q}{l_j}\delta_{jk}\delta_{mn}\delta_{m'n'}, \tag{9.135}$$

where the summation index G represents all possible group elements and l_j is the dimensionality of $\boldsymbol{\Gamma}^{(j)}$.

Proof First, consider the case where the two representations are inequivalent, for which one can construct the following matrix:

$$\mathbf{M} = \sum_G \boldsymbol{\Gamma}^{(k)}(G)\mathbf{X}\boldsymbol{\Gamma}^{(j)}(G^{-1}), \tag{9.136}$$

where $\mathbf{\Gamma}^{(k)}(G)$ is a $l_k \times l_k$ matrix, $\mathbf{\Gamma}^{(j)}(G^{-1})$ is a $l_j \times l_j$ matrix, and $\mathbf{X}$ is an arbitrary matrix with l_k row and l_j column. Then, for a certain element S of the group, it is straightforward to show the following identities:

$$\begin{aligned}
\mathbf{\Gamma}^{(k)}(S)\mathbf{M} &= \sum_G \mathbf{\Gamma}^{(k)}(S)\mathbf{\Gamma}^{(k)}(G)\mathbf{X}\mathbf{\Gamma}^{(j)}(G^{-1}) \\
&= \sum_G \mathbf{\Gamma}^{(k)}(S)\mathbf{\Gamma}^{(k)}(G)\mathbf{X}\mathbf{\Gamma}^{(j)}(G^{-1})\mathbf{\Gamma}^{(j)}(S^{-1})\mathbf{\Gamma}^{(i)}(S) \\
&= \sum_G \mathbf{\Gamma}^{(k)}(SG)\mathbf{X}\mathbf{\Gamma}^{(j)}(G^{-1}S^{-1})\mathbf{\Gamma}^{(k)}(S) \\
&= \sum_{SG} \mathbf{\Gamma}^{(k)}(SG)\mathbf{X}\mathbf{\Gamma}^{(j)}((SG)^{-1})\mathbf{\Gamma}^{(k)}(S) \\
&= \sum_G \mathbf{\Gamma}^{(k)}(G)\mathbf{X}\mathbf{\Gamma}^{(j)}((G)^{-1})\mathbf{\Gamma}^{(k)}(S) = \mathbf{M}\mathbf{\Gamma}^{(k)}(S).
\end{aligned} \tag{9.137}$$

In the last equality of the above equation, Theorem 9.1 was used. According to the Theorem 9.5, Eq. (9.137) implies that $\mathbf{M} = 0$ for $l_1 \neq l_2$ or the two representations are not equivalent for $l_1 = l_2$. Thus,

$$[\mathbf{M}]_{nm'} = 0 = \sum_G \sum_{pq} [\mathbf{\Gamma}^{(k)}(G)]_{np}\mathbf{X}_{pq}[\mathbf{\Gamma}^{(j)}(G)]_{qm'}. \tag{9.138}$$

Now, consider the case where the elements of the matrix $\mathbf{X}$ are zero except for the $n'm$ element as follows: $\mathbf{X}_{pq} = \delta_{pn'}\delta_{qm}$. Then, the above relation becomes the following identity:

$$\sum_G [\mathbf{\Gamma}^{(k)}(G)]_{nn'}[\mathbf{\Gamma}^{(j)}(G)]_{mm'} = 0, \tag{9.139}$$

which completes the proof for the cases where $l_j \neq l_k$ or the two representations are not equivalent while $l_j = l_k$.

Now, let us consider the case where the two representations are equivalent. Thus, let us drop the superscript j and k. Then,

$$\mathbf{M} = \sum_G \mathbf{\Gamma}(G)\mathbf{X}\mathbf{\Gamma}(G^{-1}) = c\mathbf{I}. \tag{9.140}$$

Therefore, considering the mm' element of the above identity, we obtain

$$\sum_{pq} \sum_G [\mathbf{\Gamma}(G)]_{mp}[\mathbf{X}]_{pq}[\mathbf{\Gamma}(G^{-1})]_{qm'} = c\delta_{mm'}. \tag{9.141}$$

Let us consider the case where $[\mathbf{X}]_{pq} = \delta_{pn}\delta_{qn'}$. Then,

$$\sum_G [\mathbf{\Gamma}(G)]_{mn}[\mathbf{\Gamma}(G^{-1})]_{n'm'} = c\delta_{mm'}. \tag{9.142}$$

Summing the above elements over $m = m'$, we thus obtain

$$\sum_m \sum_G [\mathbf{\Gamma}(G)]_{mn}[\mathbf{\Gamma}(G^{-1})]_{n'm} = cl_j. \tag{9.143}$$

On the other hand, the lefthand side of the above is equal to $Q\delta_{nn'}$ as follows.

$$\sum_G \sum_m \sum_G [\mathbf{\Gamma}(G)]_{mn}[\mathbf{\Gamma}(G^{-1})]_{n'm} = \sum_G \sum_G [\mathbf{\Gamma}(G^{-1}G)]_{n'n} = Q\delta_{n'n}. \tag{9.144}$$

Therefore, $c = \delta_{nn'}Q/l_j$. As a result,

$$\sum_G [\mathbf{\Gamma}(G)]_{mn}[\mathbf{\Gamma}(G^{-1})]_{n'm'} = \sum_G [\mathbf{\Gamma}(G)]_{mn}[\mathbf{\Gamma}(G)]^*_{m'n'} = \frac{Q}{l_j}\delta_{mm'}\delta_{nn'}, \tag{9.145}$$

where the fact that $\mathbf{\Gamma}$ is a unitary irreducible representation was used. □

Exercise Problems with Solutions

9.1 Write down the ground electronic configuration for B_2^-, determine its bond order, and the term for the ground electronic state. Use KK for the core shell.

Solution 9.1 For B_2^-, which has 11 electrons, the configuration is as follows:

$$\mathrm{KK}(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p_{x,y})^3.$$

The bond order for this is 3/2. The molecular terms for this is the same as $(\pi_u 2p_{x,y})^1$, for which the only and the ground state term is $^2\Pi_u$.

9.2 Answer the following questions for the electronic states of N_2^+.

(a) Write down the ground electronic configuration for N_2^+, determine its bond order, and the term for ground electronic state.
(b) Assume that an electron in the $\pi_u 2p_{x,y}$ orbital of the ground electronic configuration gets excited to a $2\pi_g 2p_{x,y}$ orbital. Write down all possible term symbols for the resulting excited state configuration. Among these, list all the states to which the transition from the ground state is allowed. For each allowed transition, state the appropriate selection rule clearly.

Solution 9.2

(a) The ground electronic configuration of N_2^+ is as follows:

$$\mathrm{KK}(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p_{x,y})^4(\sigma_g 2p_z)^1$$

For this configuration, $BO = 5/2$. Since all MOs are fully filled except for $\sigma_g 2p_z$, which is singly filled, there is only one term for this as follows: $^2\Sigma_g^+$.

(b) The corresponding excited state configuration is as follows:

$$\mathrm{KK}(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p_{x,y})^3(\sigma_g 2p_z)^1(\pi_g 2p_{x,y})^1$$

This is equivalent to the following:

$$(\pi_u 2p_{x,y})^1(\sigma_g 2p_z)^1(\pi_g 2p_{x,y})^1$$

Since there are three electrons occupying three different orbitals, all possible combinations of Λ and S can be used. First, summing the states of two electrons occupying $\pi_u 2p_{x,y}$ and $\sigma_g 2p_z$ respectively, we obtain

$$\Lambda = 1;\ \ S = 0, 1$$

Summing these with the state of the electron occupying $\pi_g 2p_{x,y}$, we obtain

$$\Lambda = 0,\ 2;\ S = \frac{1}{2},\ \frac{3}{2}$$

All states have u symmetry. Therefore, the resulting molecular term symbols are as follows:

$$^2\Sigma_u^{\pm},\ ^4\Sigma_u^{\pm}$$
$$^2\Delta_u,\ ^4\Delta_u$$

Among the above terms, transition from the ground state $^2\Sigma_g^+$ to the following state are allowed:

$$^2\Sigma_u^{\pm}$$

9.3 The π-type molecular orbital of a (noncyclic) propyl anion, $CH_2CHCH_2^-$, is given by the linear combination of the three carbon 2p-orbitals as follows:

$$|\psi\rangle = C_1|2p_{z1}\rangle + C_2|2p_{z2}\rangle + C_3|2p_{z3}\rangle,$$

where 1, 2, and 3 denote carbon atoms from the left to the right. For the molecular Hamiltonian $\hat{H}$,

$$\langle 2p_{z1}|\hat{H}|2p_{z1}\rangle = \langle 2p_{z2}|\hat{H}|2p_{z2}\rangle = \langle 2p_{z3}|\hat{H}|2p_{z3}\rangle = \alpha,$$
$$\langle 2p_{z1}|\hat{H}|2p_{z2}\rangle = \langle 2p_{z2}|\hat{H}|2p_{z3}\rangle = \beta.$$

Assume that $\langle 2p_{z1}|\hat{H}|2p_{z3}\rangle = 0$ and that all overlap integrals between different orbitals are zero. Use the variational principle and determine three MOs and their energies, and determine the total π-electron energy of propyl anion.

Solution 9.3 Applying the variational principle, we obtain the following matrix equation:

$$\begin{pmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}.$$

This is possible for non-zero the C_k only if the determinant is zero as follows:

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = (\alpha - E)^3 - 2\beta^2(\alpha - E)$$
$$= (\alpha - E)(\alpha - E - \sqrt{2}\beta)(\alpha - E + \sqrt{2}\beta) = 0.$$

Thus, there are the following three solutions for the energy: $E = \alpha, \alpha - \sqrt{2}\beta$, and $\alpha + \sqrt{2}\beta$. The coefficients for MO can be determined by plugging each value of E into the above matrix equation and also using the normalization condition.

For $E = \alpha$, $\beta C_2 = 0$, $\beta(C_1 + C_3) = 0$. This means that $C_2 = 0$ and $C_1 = -C_3$. Using the normalization condition, we find that

$$|\psi_n\rangle = \frac{1}{\sqrt{2}}\left(|2p_{z1}\rangle - |2p_{z3}\rangle\right).$$

For $E = \alpha - \sqrt{2}\beta$, two independent equations are $\sqrt{2}C_1 + C_2 = 0$ and $C_2 + \sqrt{2}C_3 = 0$, which result in $C_1 = -C_2/\sqrt{2}$ and $C_3 = -C_2/\sqrt{2}$. C_2 can then be determined by normalization condition. Thus,

$$|\psi_-\rangle = \frac{1}{\sqrt{2}}|2p_{z1}\rangle - \frac{1}{\sqrt{2}}|2p_{z2}\rangle + \frac{1}{2}|2p_{z3}\rangle.$$

For $E = \alpha + \sqrt{2}\beta$, two independent equations are $-\sqrt{2}C_1 + C_2 = 0$ and $C_2 - \sqrt{2}C_3 = 0$, which result in $C_1 = C_2/\sqrt{2}$ and $C_3 = C_2/\sqrt{2}$. C_2 can then be determined by normalization condition. Thus,

$$|\psi_+\rangle = \frac{1}{\sqrt{2}}|2p_{z1}\rangle + \frac{1}{\sqrt{2}}|2p_{z2}\rangle + \frac{1}{2}|2p_{z3}\rangle.$$

The four π electrons occupy $|\psi_+\rangle$ and $|\psi_n$. Thus the π-electron energy is as follows:

$$E_\pi = 2(\alpha + \sqrt{2}\beta) + 2\alpha = 4\alpha + 2\sqrt{2}\beta.$$

9.4 For 1,3-butadienyl anion, $[CH_2 = CH - CH = CH_2]^{-1}$, the four LCAO-MO π orbitals formed by p_z orbitals of carbon atoms, within the Hückel approximation, have the following energies: $\alpha \pm \beta(\sqrt{5} \pm 1)/2$, where α is the energy of each p_z orbital and β is the resonance integral between neighboring p_z orbitals. Find out the expressions for the total π orbital energy and for the total π-bonding delocalization energy.

Solution 9.4 There are five electrons occupying π MOs. Below are the three MO energies from the lowest and the number of electrons in parenthesis.

$$\alpha + \beta\frac{\sqrt{5}+1}{2}\ (2);\ \ \alpha + \beta\frac{\sqrt{5}-1}{2}\ (2);\ \alpha - \beta\frac{\sqrt{5}-1}{2}(1)$$

Summing the above for all five electrons,

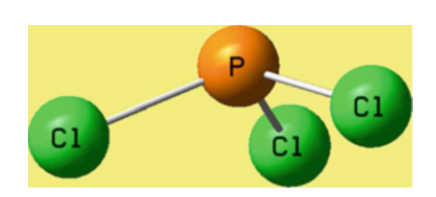
$$E_\pi = 5\alpha + \beta\frac{3\sqrt{5}+1}{2}.$$

The π orbital delocalization energy is given by

$$E_{\pi-deloc} = E_\pi - 5(\alpha + \beta) = \beta\frac{3\sqrt{5}-9}{2}.$$

The above quantity is positive, which means that there is no stabilization within the Hückel approximation.

9.5 The molecule PCl_3 shown below, where all the $P - Cl$ distances are the same and all the $Cl - P - Cl$ angles are the same, belongs to C_{3v} point group.



Use the character table below to answer questions below.

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z, x^2+y^2, z^2
A_2	1	1	−1	R_z
E	2	−1	0	$(x, y), (R_x, R_y), (x^2-y^2, xy), (xz, yz)$

(a) The reducible representation of the 12-dimensional coordinates of all atomic displacements of PCl_3 is found to be $\Gamma = 3A_1 + A_2 + 4E$. Complete the values of characters for this reducible representation in the table below.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ			

(b) Identify all the irreducible representations constituting the vibrational modes.
(c) How many IR active modes are and what are their irreducible representations?
(d) How many Raman active modes are and what are their irreducible representations?

Solution 9.5

(a) Making the linear combination of characters for each symmetry operation, we obtain the following components for the table.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ	12	0	2

The above elements can be confirmed to produce the given linear combination as follows:

$$A_1: \frac{1}{6}(12 \cdot 1 + 2 \cdot 0 \cdot 1 + 3 \cdot 2 \cdot 1) = 3$$

$$A_2: \frac{1}{6}(12 \cdot 1 + 2 \cdot 0 \cdot 1 + 3 \cdot 2 \cdot (-1)) = 1$$

$$E: \frac{1}{6}(12 \cdot 2 + 2 \cdot 0 \cdot (-1) + 3 \cdot 2 \cdot 1) = 4$$

(b) From the character table, it is clear that

$$R_{tr} = A_1 + E,$$

$$R_{rot} = A_2 + E.$$

Therefore,

$$\Gamma_{vib} = \Gamma - \Gamma_{tr} - \Gamma_{rot} = 3A_1 + A_2 + 4E - (A_1 + A_2 + 2E) = 2A_1 + 2E.$$

(c) and (d): There are 6 vibrational modes, which are all IR and Raman active according to their symmetry properties.

9.6 Express a reducible representation Γ, for which the values of characters are shown in the following character table for D_3, in terms of all irreducible representations and identify all possible candidates for irreducible representations that are IR and Raman active vibrational modes.

D_3	E	$2C_3$	$3C_2$		
A_1	1	1	1	$z^2, x^2 + y^2$	
A_2	1	1	-1	z	R_z
E	2	-1	0	$(x, y), (x^2 - y^2, xy), (xz, yz)$	(R_x, R_y)
Γ	12	0	-2		

Solution 9.6 Each component of Γ is as follows:

$$A_1 : \frac{1}{6}(12 - 6) = 1; \qquad A_2 : \frac{1}{6}(12 + 6) = 3; \qquad E : \frac{1}{6}(2 \cdot 12) = 4$$

Therefore, $\Gamma = A_1 + 3A_2 + 4E$. Since $\Gamma_{tr} = A_2 + E$ and $\Gamma_R = A_2 + E$, $\Gamma_{vib} = \Gamma - \Gamma_{tr} - \Gamma_R = A_1 + A_2 + 2E$. Out of these five modes belonging to A_2 and E are IR active, and five modes belonging to A_1 and E are Raman active.

Problems

9.7 Write down the ground electronic configuration for C_2^+, corresponding bond order, and all possible electronic terms. If an electron in $\sigma_u 2s$ of this configuration becomes excited to $\pi_g 2p_{x,y}$, what are possible terms corresponding to the excited electronic configuration?

9.8 For 1,3-butadiene cation, $[C_4H_6]^+$, what is the π-orbital delocalization energy within the Hückel approximation? Express your answer in terms of $\alpha = H_{ii}$ and $\beta = H_{i,i+1}$.

9.9 The molecule allene ($H_2C = C = CH_2$) belongs to a point group D_{2d}. Draw the molecule and indicate all the symmetry elements. Assume that hydrogen atoms are rigidly fixed to carbon atoms. Then, find out reducible representation of the molecule in the basis of 9 dimensional coordinates of carbon atoms only. Express this as the sum of irreducible representations and identify all IR and Raman active modes.

Chapter 10
Quantum Dynamics of Pure and Mixed States



Whatever Nature has in store for mankind, unpleasant as it may be, men must accept, for ignorance is never better than knowledge.

— Enrico Fermi

Abstract This chapter provides an overview of quantum dynamics and its approximations. For pure states that can be represented by a linear combination of kets/bras (or wavefunctions), this entails solving the time dependent Schrödinger equation. Three major pictures of the dynamics, Schrödinger picture, Heisenberg picture, and interaction picture are explained first. Then, the interaction picture is used for the description of time dependent perturbation theory, and Fermi's golden rule is derived from the first order approximation. For the description of more general mixed states, introduction of density operator and extension of the time dependent Schrödinger equation to the quantum Liouville equation become necessary. Application of the perturbation theory to this quantum Liouville equation is presented as well.

So far, the focus has been on stationary (time independent) properties of a closed quantum system and a pure quantum state that can be expressed by a single ket (bra) or wavefunction. While this has been enough for explaining the foundational aspects of quantum mechanics and applications to well-isolated molecular properties, it is limited for quantitative understanding of time dependent quantities and properties of a large collection of molecules that are interacting with each other. Most chemical phenomena involve understanding these dynamical processes in complex environments. For this, explicit consideration of quantum dynamics and general approaches to represent mixed states are necessary. This chapter describes basic principles governing the dynamics of pure and mixed states, and simple approximations.

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10.1 Quantum Dynamics of Pure States

A pure quantum state refers to any single quantum mechanical state that can be represented by a ket (bra) or a linear superposition of kets (bras). As described briefly in Chap. 2, for a closed quantum system with a Hamiltonian operator $\hat{H}$, the pure state at time t can be determined completely by solving the time dependent Schrödinger equation, Eq. (2.43). Given that the initial state is $|\psi\rangle$, the solution of the time dependent Schrödinger equation can be expressed in terms of the time evolution operator $\hat{U}_H(t)$ defined by Eq. (2.82). The resulting expression, Eq. (2.85), can again be expressed in a number of different ways as follows:

$$
\begin{aligned}
|\psi; t\rangle = \hat{U}_H(t)|\psi\rangle &= \exp\left\{-\frac{i}{\hbar}\hat{H}t\right\}|\psi\rangle \\
&= \left\{\sum_{n=0}^{\infty}\frac{1}{n!}\left(-\frac{it}{\hbar}\right)^n \hat{H}^n\right\}|\psi\rangle. \qquad (10.1)
\end{aligned}
$$

In the limit of $t = 0$, the above expression approaches the limit of $|\psi; t = 0\rangle = |\psi\rangle$ as it should.

Given the time dependent state as expressed above, the corresponding time dependent expectation value at time t of any physical observable $\hat{A}$, which is assumed to be time independent for now, is equal to

$$
\langle\hat{A}\rangle_t = \langle\psi; t|\hat{A}|\psi; t\rangle. \qquad (10.2)
$$

While this view of the quantum dynamics is sufficient for describing all the time dependent processes in quantum mechanics and is most widely used, it turns out to be just one of many possible "pictures" of the dynamics known as the Schrödinger picture. In this picture, the time evolution of the system is viewed as being entirely due to the change of the state from $|\psi\rangle$ to $|\psi; t\rangle$ although there can still be an additional time dependence of an operator $\hat{A}$ due to extrinsic factors. To make this clear, let us denote the operator in the Schrdinger picture with subscript "S" and also assume the possibility of additional time dependence that cannot be explained in terms of time evolving quantum states in the Schrödinger picture. Thus, the general time dependent expectation value of any time dependent physical observable can be expressed as

$$
\langle\hat{A}(t)\rangle_t = \langle\psi; t|\hat{A}_S(t)|\psi; t\rangle. \qquad (10.3)
$$

Taking the time derivative, we find that the above time dependent expectation value satisfies the following differential equation:

$$\begin{aligned}\frac{d}{dt}\langle\hat{A}(t)\rangle_t &= \left(\frac{\partial}{\partial t}\langle\psi;t|\right)\hat{A}_S(t)|\psi;t\rangle + \langle\psi;t|\hat{A}_S(t)\left(\frac{\partial}{\partial t}|\psi;t\rangle\right)\\ &\quad+\langle\psi;t|\left(\frac{\partial}{\partial t}\hat{A}_S(t)\right)|\psi;t\rangle\\ &= \frac{i}{\hbar}\langle\psi;t|\hat{H}\hat{A}_S(t)|\psi;t\rangle - \frac{i}{\hbar}\langle\psi;t|\hat{A}_S(t)\hat{H}|\psi;t\rangle\\ &\quad+\langle\psi;t|\left(\frac{\partial}{\partial t}\hat{A}_S(t)\right)|\psi;t\rangle\\ &= \langle\psi;t|\left(\frac{i}{\hbar}[\hat{H},\hat{A}_S(t)] + \frac{\partial}{\partial t}\hat{A}_S(t)\right)|\psi;t\rangle.\end{aligned} \tag{10.4}$$

10.1.1 Heisenberg Picture

Heisenberg viewed that the dynamics is entirely due to time evolving physical observables whereas the state remains the same. This is known as the Heisenberg picture and can easily be shown to be equivalent to the Schrödinger picture. For any time dependent operator in the Schrödinger picture $\hat{A}_S(t)$, we can define the following time dependent operator in the Heisenberg picture:

$$\hat{A}_H(t) = \hat{U}_H^\dagger(t)\hat{A}_S(t)\hat{U}_H(t). \tag{10.5}$$

Then, the expectation value of $\hat{A}(t)$ at time t can be viewed as the expectation of the above operator with respect to the time independent state $|\psi\rangle$ as follows:

$$\langle\hat{A}(t)\rangle_t = \langle\psi|\hat{A}_H(t)|\psi\rangle = \langle\psi|\hat{U}_H^\dagger(t)\hat{A}_S(t)\hat{U}_H(t)|\psi\rangle = \langle\psi;t|\hat{A}_S(t)|\psi;t\rangle, \tag{10.6}$$

where the second equality shows the equivalence of the two pictures.

In the Heisenberg picture, all the time dependent properties are directly encoded into time evolving operators as if physical observables evolve in time in classical mechanics. This is represented by the time evolution equation for the time dependent

operator as follows:

$$\begin{aligned}\frac{d}{dt}\hat{A}_H(t) &= \frac{i}{\hbar}\hat{H}\hat{U}_H^\dagger(t)\hat{A}_S(t)\hat{U}_H(t) - \frac{i}{\hbar}\hat{U}_H^\dagger(t)\hat{A}_S(t)\hat{U}_H(t)\hat{H} \\ &\quad +\hat{U}_H^\dagger(t)\left(\frac{\partial}{\partial t}\hat{A}_S(t)\right)\hat{U}_H(t) \\ &= \frac{i}{\hbar}[\hat{H}, \hat{A}_H(t)] + \hat{U}_H^\dagger(t)\left(\frac{\partial}{\partial t}\hat{A}_S(t)\right)\hat{U}_H(t). \end{aligned} \tag{10.7}$$

For the case where $\hat{A}_S(t)$ commutes with the Hamiltonian $\hat{H}$, it also commutes with the time evolution operator $\hat{U}_H(t)$. For this case, $\hat{A}_H(t) = \hat{A}_S(t)$, and the time derivative of $\hat{A}_H(t)$ is the same as the partial derivative of $\hat{A}_S(t)$ with respect to time.

In the Heisenberg picture, the relationship between time dependent position and momentum operators are similar to those for classical mechanics. For this, let us consider the case of the following one dimensional Hamiltonian:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x}).$$

Then, the time derivatives of the position and momentum operators in the Heisenberg picture are as follows:

$$\begin{aligned}\frac{d}{dt}\hat{x}_H(t) &= \frac{i}{\hbar}[\hat{H}, \hat{x}_H(t)] = \hat{U}_H^\dagger(t)\frac{i}{\hbar}[\hat{H}, \hat{x}]\hat{U}_H(t) \\ &= \hat{U}_H^\dagger(t)\frac{i}{\hbar}[\frac{\hat{p}^2}{2m}, \hat{x}]\hat{U}_H(t) \\ &= \frac{\hat{p}_H(t)}{m}, \end{aligned} \tag{10.8}$$

$$\begin{aligned}\frac{d}{dt}\hat{p}_H(t) &= \frac{i}{\hbar}[\hat{H}, \hat{p}_H(t)] = \hat{U}_H^\dagger(t)\frac{i}{\hbar}[\hat{H}, \hat{p}]\hat{U}_H(t) \\ &= \hat{U}_H^\dagger(t)\frac{i}{\hbar}[\hat{V}(\hat{x}), \hat{p}]\hat{U}_H(t) \\ &= \hat{U}_H^\dagger(t)\left(-\hat{V}'(\hat{x})\right)\hat{U}_H(t) = \hat{F}_H(t). \end{aligned} \tag{10.9}$$

In the above expression, $\hat{V}'(\hat{x})$ implies the derivative of the potential energy with its argument as the position operator and the fact that $[\hat{p}, f(\hat{x})] = -i\hbar f'(\hat{x})$ for any function of position $f(x)$ has been used. Thus, $\hat{F}_H(t)$ is the time dependent force operator in the Heisenberg picture.

For the case of a harmonic oscillator with $V(x) = m\omega^2 x^2/2$, the force operator is proportional to position as follows: $\hat{F}_H(t) = -m\omega^2 \hat{x}_H(t)$. Therefore, Eq. (10.9) reduces to

$$\frac{d}{dt}\hat{p}_H(t) = -m\omega^2 \hat{x}_H(t). \tag{10.10}$$

This is exactly the same as the classical equation of motion for the momentum. Therefore, one can find out the solution for the time dependent position operators in terms of that for the classical mechanics as follows:

$$\hat{x}_H(t) = \hat{x}\cos(\omega t) + \frac{\hat{p}}{m\omega}\sin(\omega t), \tag{10.11}$$

$$\hat{p}_H(t) = \hat{p}\cos(\omega t) - m\omega\hat{x}\sin(\omega t). \tag{10.12}$$

10.1.2 Interaction Picture and Time Dependent Perturbation Theory

Let us consider the case where the system is subject to additional perturbation Hamiltonian, $\hat{H}_1(t)$, which can be time dependent in general, in addition to the original zeroth order Hamiltonian, $\hat{H}_0$. Thus, the total Hamiltonian describing the system is given by

$$\hat{H}(t) = \hat{H}_0 + \hat{H}_1(t). \tag{10.13}$$

The time dependence of $\hat{H}_1(t)$ may originate from any source, but the most typical one is the application of time dependent field.

In the Schrödinger picture, the state evolves according to the following time dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}|\psi; t\rangle = \hat{H}(t)|\psi; t\rangle = (\hat{H}_0 + \hat{H}_1(t))|\psi; t\rangle. \tag{10.14}$$

Given that the eigenstates and eigenvalues of $\hat{H}_0$ are known and that we want to develop perturbation theory with respect to $\hat{H}_1(t)$, it is convenient to consider a Heisenberg picture with respect to $\hat{H}_0$. This is known as the interaction picture. Thus, let us introduce the time evolution operator for $\hat{H}_0$,

$$\hat{U}_0(t) = \exp\left\{-\frac{i}{\hbar}\hat{H}_0 t\right\}, \tag{10.15}$$

which represents the dynamics of a system subject to only the zeroth order Hamiltonian $\hat{H}_0$. Note that $\hat{U}_0(t)$ is a unitary operator as follows:

$$\hat{U}_0(t)\hat{U}_0^\dagger(t) = \hat{U}_0^\dagger(t)\hat{U}_0(t) = \hat{1}. \tag{10.16}$$

We can now define the state in the interaction picture by applying $\hat{U}_0^\dagger(t)$ to $|\psi; t\rangle$ as

$$|\psi; t\rangle_I \equiv \hat{U}_0^\dagger(t)|\psi; t\rangle. \tag{10.17}$$

Then, the equation governing the time evolution of $|\psi; t\rangle_I$ is

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}|\psi; t\rangle_I &= i\hbar\left(\frac{\partial}{\partial t}\hat{U}_0^\dagger(t)\right)|\psi; t\rangle + \hat{U}_0^\dagger(t)i\hbar\frac{\partial}{\partial t}|\psi; t\rangle \\ &= -\hat{U}_0^\dagger(t)\hat{H}_0|\psi; t\rangle + \hat{U}_0^\dagger(t)\left(\hat{H}_0 + \hat{H}_1(t)\right)|\psi; t\rangle \\ &= \hat{U}_0^\dagger(t)\hat{H}_1(t)|\psi; t\rangle \\ &= \hat{H}_{1,I}(t)|\psi; t\rangle_I, \end{aligned} \tag{10.18}$$

where Eqs. (10.16) and (10.17) have been used and the following first order Hamiltonian in the interaction picture has been introduced.

$$\hat{H}_{1,I}(t) \equiv \hat{U}_0^\dagger(t)\hat{H}_1(t)\hat{U}_0(t). \tag{10.19}$$

Integrating Eq. (10.18) with respect to time, we find that

$$|\psi; t\rangle_I = |\psi; 0\rangle_I - \frac{i}{\hbar}\int_0^t dt'\hat{H}_{1,I}(t')|\psi; t'\rangle_I. \tag{10.20}$$

The above expression is nothing but the integral equation form equivalent to Eq. (10.18) but is amenable for approximate solution more easily as detailed below.

Both sides of Eq. (10.20) involve as yet unknown $|\psi; t\rangle_I$ at two different times. However, for the state in the integrand, we can substitute the definition given by the lefthand side as follows:

$$\begin{aligned} |\psi; t\rangle_I = |\psi; 0\rangle_I &- \frac{i}{\hbar}\int_0^t dt'\hat{H}_{1,I}(t')|\psi; 0\rangle_I \\ &+ \left(-\frac{i}{\hbar}\right)^2\int_0^t dt'\int_0^{t'} dt''\hat{H}_{1,I}(t')\hat{H}_{1,I}(t'')|\psi; t''\rangle_I. \end{aligned} \tag{10.21}$$

The above expression does not look simple either and appears to make getting the solution even more complicated because the unknown $|\psi; t''\rangle_I$ still exists on the righthand side, which now involves double integration with respect to time.

However, given that the magnitude of $\hat{H}_1(t)$ is small enough so that its effect becomes smaller and smaller as the order of integration increases, one can continue applying the iteration procedure and obtain the following formal solution:

$$
\begin{aligned}
|\psi; t\rangle_I = |\psi; 0\rangle_I &- \frac{i}{\hbar}\int_0^t dt' \hat{H}_{1,I}(t')|\psi; 0\rangle_I \\
&+ \left(-\frac{i}{\hbar}\right)^2 \int_0^t dt' \int_0^{t'} dt'' \hat{H}_{1,I}(t')\hat{H}_{1,I}(t'')|\psi; 0\rangle_I \\
&+ \left(-\frac{i}{\hbar}\right)^3 \int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} dt''' \hat{H}_{1,I}(t')\hat{H}_{1,I}(t'')\hat{H}_{1,I}(t''')|\psi; 0\rangle_I \\
&+ \cdots
\end{aligned}
\tag{10.22}
$$

Equation (10.22) is a general formal solution for the state in the interaction picture and is well defined as long as the infinite order limit of the sum of multiple time integrations converges. Finding out the exact condition for such convergence to be ensured is not a simple task in general. However, in many cases, the convergence can be determined at least numerically given a specific form of the Hamiltonian. Here, we consider only physically well-defined perturbations for which the convergence of perturbation terms is guaranteed.

If the effect of $\int_0^t dt' \hat{H}_{1,I}(t')/\hbar$ is very small compared to the zeroth order term, an approximation that keeps only the first order term in Eq. (10.22) is reasonable. Thus, we obtain the following first order approximation:

$$
|\psi; t\rangle_I^{(1)} = |\psi; 0\rangle_I - \frac{i}{\hbar}\int_0^t dt' \hat{H}_{1,I}(t')|\psi; 0\rangle_I . \tag{10.23}
$$

Employing the definitions of Eqs. (10.17) and (10.19), and returning to the original Schrödinger picture, we find that the above expression is equivalent to

$$
|\psi; t\rangle^{(1)} = |\psi; t\rangle^{(0)} - \frac{i}{\hbar}\int_0^t dt' e^{-\frac{i}{\hbar}\hat{H}_0(t-t')}\hat{H}_1(t')|\psi; t'\rangle^{(0)}, \tag{10.24}
$$

where

$$
|\psi; t\rangle^{(0)} = \hat{U}_0(t, 0)|\psi; 0\rangle = e^{-\frac{i}{\hbar}\hat{H}_0 t}|\psi; 0\rangle . \tag{10.25}
$$

10.1.3 Fermi's Golden Rule

Suppose we are interested in the rate of transition of the system from an eigenstate of $\hat{H}_0$ to another one due to the perturbation $\hat{H}_1(t)$. Thus, let us consider the case where the state of the system at $t = 0$ is an eigenstate of $\hat{H}_0$ with eigenvalue E_j,

which we denote as $|E_j\rangle$. Then, the first order approximation for the state at time t, Eq. (10.24), can be expressed as

$$|\psi; t\rangle^{(1)} = e^{-\frac{i}{\hbar}E_j t}|E_j\rangle - \frac{i}{\hbar}\int_0^t dt' e^{-\frac{i}{\hbar}\hat{H}_0(t-t')}\hat{H}_1(t')e^{-\frac{i}{\hbar}E_j t'}|E_j\rangle. \tag{10.26}$$

Let us denote the probability for the system at time t to have made transition to another eigenstate $|E_k\rangle$ of $\hat{H}_0$ as $P_{j\to k}(t)$. Without losing generality, we can assume that $\langle E_j|E_k\rangle = 0$. Up to the lowest order of $\hat{H}_1(t)$, this probability can be calculated by projecting the above first order time dependent perturbation approximation onto $|E_k\rangle$ and taking its absolute square as follows:

$$\begin{aligned} P_{j\to k}(t) &= \left|\langle E_k|\psi; t\rangle^{(1)}\right|^2 = \left|-\frac{i}{\hbar}\int_0^t dt' e^{-\frac{i}{\hbar}E_k(t-t')}\langle E_k|\hat{H}_1(t')|E_j\rangle e^{-\frac{i}{\hbar}E_j t'}\right|^2 \\ &= \frac{1}{\hbar^2}\int_0^t dt' \int_0^t dt'' e^{\frac{i}{\hbar}(E_k-E_j)(t'-t'')}\langle E_k|\hat{H}_1(t')|E_j\rangle\langle E_j|\hat{H}_1(t'')|E_k\rangle. \end{aligned} \tag{10.27}$$

The time derivative of the above probability can be defined as the rate of transition, which is in general time dependent and is given by

$$\begin{aligned} \Gamma_{j\to k}(t) &\equiv \frac{d}{dt}P_{j\to k}(t) \\ &= \frac{1}{\hbar^2}\left\{\int_0^t dt'' e^{\frac{i}{\hbar}(E_k-E_j)(t-t'')}\langle E_k|\hat{H}_1(t)|E_j\rangle\langle E_j|\hat{H}_1(t'')|E_k\rangle \right. \\ &\quad \left. + \int_0^t dt' e^{\frac{i}{\hbar}(E_k-E_j)(t'-t)}\langle E_k|\hat{H}_1(t')|E_j\rangle\langle E_j|\hat{H}_1(t)|E_k\rangle\right\}. \end{aligned} \tag{10.28}$$

In the integrals of the above expression, let us replace t'' with $t-\tau$ in the first term and t' with $t-\tau$ in the second term. Then,

$$\begin{aligned} \Gamma_{j\to k}(t) &= \frac{1}{\hbar^2}\left\{\int_0^t d\tau e^{\frac{i}{\hbar}(E_k-E_j)\tau}\langle E_k|\hat{H}_1(t)|E_j\rangle\langle E_j|\hat{H}_1(t-\tau)|E_k\rangle \right. \\ &\quad \left. + \int_0^t d\tau e^{-\frac{i}{\hbar}(E_k-E_j)\tau}\langle E_k|\hat{H}_1(t-\tau)|E_j\rangle\langle E_j|\hat{H}_1(t)|E_k\rangle\right\} \\ &= 2\mathrm{Re}\left[\frac{1}{\hbar^2}\int_0^t d\tau e^{\frac{i}{\hbar}(E_k-E_j)\tau}\langle E_k|\hat{H}_1(t)|E_j\rangle\langle E_j|\hat{H}_1(t-\tau)|E_k\rangle\right]. \end{aligned} \tag{10.29}$$

In the above expression, the fact that the first and second integrals in the first equality are complex conjugates of each other have been used and "Re" implies the real part.

Let us now consider the case where the matrix element of the perturbation Hamiltonian is given by

$$\langle E_k|\hat{H}_1(t)|E_j\rangle = J_{jk}e^{-i\omega t}, \tag{10.30}$$

where ω is a real number. Then, Eq. (10.29) can be expressed as

$$\begin{aligned}\Gamma_{j\to k}(t) &= \frac{2}{\hbar^2}\mathrm{Re}\left[\int_0^t d\tau e^{\frac{i}{\hbar}(E_k-E_j)\tau}J_{jk}e^{-i\omega t}J_{jk}^*e^{i\omega(t-\tau)}\right]\\ &= \frac{2|J_{jk}|^2}{\hbar^2}\mathrm{Re}\left[\int_0^t d\tau e^{\frac{i}{\hbar}(E_k-E_j)\tau}e^{-i\omega\tau}\right],\end{aligned} \tag{10.31}$$

where the fact that $\langle E_j|\hat{H}_1(t-\tau)|E_k\rangle$ is the complex conjugate of Eq. (10.30) with $t-\tau$ as time argument has been used. In the limit of $t\to\infty$, the above rate approaches the following steady state limit:

$$\begin{aligned}\Gamma_{j\to k}(\infty) &= \frac{2|J_{jk}|^2}{\hbar^2}\mathrm{Re}\left[\int_0^\infty d\tau\exp\left\{i\left(\frac{E_k-E_j}{\hbar}-\omega\right)\tau\right\}\right]\\ &= \frac{|J_{jk}|^2}{\hbar^2}\int_{-\infty}^\infty d\tau\exp\left\{i\left(\frac{E_k-E_j}{\hbar}-\omega\right)\tau\right\}\\ &= \frac{2\pi|J_{jk}|^2}{\hbar}\delta(E_k-E_j-\hbar\omega),\end{aligned} \tag{10.32}$$

where the Fourier integral definition of the delta function, Eq. (1.85), has been used.

Equation (10.32) is the simplest form of the Fermi's golden rule (FGR), and serves as the basis for calculating transition rates for many dynamical processes and for calculating intensities of spectroscopic transitions. Although this expression involves a delta function, which is singular, a physically meaningful answers can be obtained from this if the implication of taking the mathematical limit of $t\to\infty$ is taken into consideration within the proper physical context. In addition, the final states to which the transition occurs are hardly a single discrete state in many real situations. This can also be used to remove the singularity.

Let us consider the case where $\hat{H}_1(t)$ represents the interaction of an electric field and a molecule with transition dipole $\boldsymbol{D}_{jk}$. In this case, within the dipole approximation[1] and the rotating wave approximation,[2] the perturbation Hamiltonian

[1] This is to assume that there is no spatial variance of the filed at molecular length scale. See Appendix of this chapter for more details.

[2] This is to ignore highly oscillating non-resonant term between field and transition. See Appendix of this chapter for more details.

can be expressed as

$$\hat{H}_1(t) = \mathcal{A}(\boldsymbol{D}_{jk} \cdot \mathbf{u}_e)|E_k\rangle\langle E_j|e^{-i\omega t} + \mathcal{A}^*(\boldsymbol{D}_{jk} \cdot \mathbf{u}_e)^*|E_j\rangle\langle E_k|e^{i\omega t}, \tag{10.33}$$

where ω is the frequency of the radiation, and $\mathcal{A}$ and $\mathbf{u}_e$ are the amplitude and unit polarization vector of its electric field component. For this case, Eq. (10.32) reduces to

$$\Gamma^s_{jk}(\omega) = \frac{2\pi|\mathcal{A}|^2|\boldsymbol{D}_{jk} \cdot \mathbf{u}_e|^2}{\hbar}\delta(E_k - E_j - \hbar\omega), \tag{10.34}$$

which gives the intensity of the transition at frequency ω. In this expression, $\delta(E_k - E_j - \hbar\omega)$ can be viewed as an idealization of a narrow peak centered at $\omega = (E_k - E_j)/\hbar$.

Let us consider another common case where the FGR rate expression, Eq. (10.32), leads to a more well-defined rate. Assume that the final states are not in fact a single state but a set of states and assume also that $\omega = 0$ in Eq. (10.30) for simplicity. The FGR rate in this case becomes the sum of all rates given by Eq. (10.32) over all possible final states as follows:

$$\Gamma_{FGR}^{j\to S_f} = \sum_{k\in S_f} \frac{2\pi|J_{jk}|^2}{\hbar}\delta(E_k - E_j). \tag{10.35}$$

Let us also assume that the final states form a continuum with distribution $w_f(E_f, \xi_f)$ such that

$$\sum_{k\in S_f} = \int dE_k \int d\xi_f w_f(E_k, \xi_f), \tag{10.36}$$

where ξ_f collectively represents the set of additional quantum numbers needed to completely specify each of the final states in the set S_f. Employing the above relationship in Eq. (10.35) and then conducting the integration over E_k, we then obtain the following rate expression:

$$\begin{aligned}\Gamma_{FGR}^{j\to S_f} &= \int dE_k \int d\xi_f w_f(E_k, \xi_f)\frac{2\pi|J_{jk}(\xi_f)|^2}{\hbar}\delta(E_k - E_j) \\ &= \int d\xi_f \frac{2\pi|J_{jk}(\xi_f)|^2}{\hbar} w_f(E_j, \xi_f),\end{aligned} \tag{10.37}$$

where we have included the general case where J_{jk} depends on ξ_f. In a simple case where J_{jk} is independent of ξ_f, which is now denoted as J_{jf}, the above expression

can be simplified further to

$$\Gamma_{FGR}^{j\to S_f} = \frac{2\pi|J_{jf}|^2}{\hbar}\rho_f(E_j), \tag{10.38}$$

where $\rho_f(E_j) = \int d\xi_f w_f(E_j, \xi_f)$ is the final density of states at E_j.

10.2 Quantum Dynamics of Mixed Quantum States

So far, we have assumed that a complete information on the quantum state of the system is available. This is hardly the case in reality. In addition to the intrinsic quantum uncertainty, there always exist additional uncertainties at practical level due to imprecision, disorder, and lack of full information on conditions determining the states. Systems of these characteristics are in mixed quantum states and need to be treated at the level of a density operator.

10.2.1 Density Operator and Quantum Liouville Equation

The concept of the density operator is more general than quantum states we considered so far and requires both ket and bra for its definition. Any pure quantum state can be represented by a density operator. Consider a quantum state $|\psi\rangle$. Then, the density operator corresponding to this state is as follows:

$$\hat{\rho}_\psi = |\psi\rangle\langle\psi|. \tag{10.39}$$

If the system is governed by a Hamiltonian $\hat{H}$, then the state prepared in $|\psi\rangle$ at time $t = 0$ evolves to become $|\psi; t\rangle = \hat{U}_H(t)|\psi\rangle$ at time t. For the definition of the density operator to be consistent at all time, given that it is defined as above at time $t = 0$, it should at time t become

$$\hat{\rho}_\psi(t) = |\psi; t\rangle\langle\psi; t| = \hat{U}_H(t)|\psi\rangle\langle\psi|\hat{U}_H^\dagger(t). \tag{10.40}$$

Taking the time derivative of the above density operator, then we find that

$$\begin{aligned}\frac{\partial}{\partial t}\hat{\rho}_\psi(t) &= -\frac{i}{\hbar}\hat{H}\hat{U}_H(t)|\psi\rangle\langle\psi|\hat{U}_H^\dagger(t) + \frac{i}{\hbar}\hat{U}_H(t)|\psi\rangle\langle\psi|\hat{U}_H^\dagger(t)\hat{H} \\ &= -\frac{i}{\hbar}[\hat{H}, \hat{\rho}_\psi(t)].\end{aligned} \tag{10.41}$$

The above equation is an example of the quantum Liouville equation, which can be shown to be valid for any density operator.

Now, let us consider an example of a mixed quantum state. Assume that we know the system is either in state $|\psi_1\rangle$ or $|\psi_2\rangle$, but do not know exactly which state the system is in. The only information available is that their respective probabilities are p_1 and p_2. This kind of situation is completely different from the case where the state is given by a linear combination of $|\psi_1\rangle$ and $|\psi_2\rangle$ that is still a pure state, and can be represented by the following density operator:

$$\hat{\rho} = p_1|\psi_1\rangle\langle\psi_1| + p_2|\psi_2\rangle\langle\psi_2|, \tag{10.42}$$

where it is assumed that $|\psi_1\rangle$ and $|\psi_2\rangle$ are normalized. In the above expression, $p_1 + p_2 = 1$, while $p_1, p_2 \geq 0$. Note that the two states $|\psi_1\rangle$ and $|\psi_2\rangle$ do not have to be orthogonal to each other. Since the possibilities for the system to be in either of these two states are completely uncorrelated, the above density operator should at time t become

$$\begin{aligned}\hat{\rho}(t) &= p_1|\psi_1; t\rangle\langle\psi_1; t| + p_2|\psi_2; t\rangle\langle\psi_2; t| \\ &= p_1\hat{U}_H(t)|\psi_1\rangle\langle\psi_1|\hat{U}_H^\dagger(t) + p_2\hat{U}_H(t)|\psi_2\rangle\langle\psi_2|\hat{U}_H^\dagger(t) \\ &= \hat{U}_H(t)\hat{\rho}\hat{U}_H^\dagger(t).\end{aligned} \tag{10.43}$$

The above expression suggests that the manner of time evolution for the density operator is independent of whether it represents the pure or mixed state as long as the governing Hamiltonian is the same.

Extending the concept of the mixed state illustrated above to more general cases that involve more than two states, we can now define a general density operator,

$$\hat{\rho} = \sum_j p_j|\psi_j\rangle\langle\psi_j|, \tag{10.44}$$

where each $|\psi_j\rangle$ is normalized and $p_j \geq 0$ represents the probability for the system to be in state $|\psi_j\rangle$. Thus, $\sum_j p_j = 1$. It is obvious that the density operator defined in this way is always Hermitian. In addition, for any state $|\varphi\rangle$, $\langle\varphi|\hat{\rho}|\varphi\rangle$ is always nonnegative. This means that the diagonal elements of any density operator in any basis, which are probabilities to find the system in those states, are always nonnegative.

For the density operator given by Eq. (10.44) at time $t = 0$, the density operator at time t becomes

$$\hat{\rho}(t) = \hat{U}_H(t)\hat{\rho}\hat{U}_H^\dagger(t), \tag{10.45}$$

which satisfies the following quantum Liouville equation:

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}\left[\hat{H}, \hat{\rho}(t)\right] \equiv -i\hat{\mathcal{L}}\hat{\rho}(t). \tag{10.46}$$

The second equality in the above equation serves as the definition of $\hat{\mathcal{L}}$, a super-operator[3] called quantum Liouvillian.

Given the mixture of states $|\psi_j\rangle$, each with probability p_j, the expectation value of any physical observable $\hat{A}$ should be

$$\langle\hat{A}\rangle = \sum_j p_j\langle\psi_j|\hat{A}|\psi_j\rangle. \tag{10.47}$$

It turns out that the above quantity can be calculated in terms of the density operator $\hat{\rho}$ given by Eq. (10.44) as follows:

$$\langle\hat{A}\rangle = Tr\left\{\hat{A}\hat{\rho}\right\}, \tag{10.48}$$

where $Tr\{\cdots\}$ implies sum of all the diagonal elements of $\cdots$ calculated for any complete basis. More detailed description of the trace operation and its properties are provided below.

Definition and Invariance of Trace

Given an operator $\hat{A}$ and a complete basis, $|\phi_n\rangle$, with respect to which the operator can be represented, the trace of $\hat{A}$ is defined as the sum of all the diagonal elements as follows:

$$Tr\left\{\hat{A}\right\} = \sum_n\langle\phi_n|\hat{A}|\phi_n\rangle. \tag{10.49}$$

There are two important properties of trace operation that can be proved easily using the completeness relation, $\sum_n|\phi_n\rangle\langle\phi_n| = \hat{1}$.

- The trace of the product of two operators, $\hat{A}$ and $\hat{B}$, is independent of the order as follows.

$$Tr\left\{\hat{A}\hat{B}\right\} = Tr\left\{\hat{B}\hat{A}\right\}. \tag{10.50}$$

(continued)

[3] Super-operator refers to an operator that operates on quantum mechanical operators. In this case, note that $\mathcal{L}$ operates on the density operator.

The proof of this is as follows:

$$\begin{aligned} Tr\left\{\hat{A}\hat{B}\right\} &= \sum_n \langle\phi_n|\hat{A}\hat{B}|\phi_n\rangle \\ &= \sum_n\sum_m \langle\phi_n|\hat{A}|\phi_m\rangle\langle\phi_m|\hat{B}|\phi_n\rangle \\ &= \sum_n\sum_m \langle\phi_m|\hat{B}|\phi_n\rangle\langle\phi_n|\hat{A}|\phi_m\rangle \\ &= \sum_m \langle\phi_m|\hat{B}\hat{A}|\phi_m\rangle = Tr\left\{\hat{B}\hat{A}\right\}, \end{aligned} \tag{10.51}$$

where the fact that $|\phi_n\rangle$ form a complete basis has been used in the second and the fourth equalities.

- Given an operator $\hat{A}$ and its unitary transformation $\hat{A}' = \hat{U}^\dagger\hat{A}\hat{U}$, the traces of $\hat{A}$ and $\hat{A}'$ are always the same. This is a direct outcome of Eq. (10.50) as shown below.

$$Tr\{\hat{A}'\} = Tr\{\hat{U}^\dagger\hat{A}\hat{U}\} = Tr\{\hat{A}\hat{U}\hat{U}^\dagger\} = Tr\{\hat{A}\}, \tag{10.52}$$

where the fact that $\hat{U}\hat{U}^\dagger = \hat{1}$ has been used.

Having defined the trace operation and its two invariance properties, we can easily prove the equivalence of Eqs. (10.47) and (10.48) as follows:

$$\begin{aligned} Tr\left\{\hat{A}\hat{\rho}\right\} &= \sum_n \langle\phi_n|\hat{A}\hat{\rho}|\phi_n\rangle \\ &= \sum_n\sum_j p_j\langle\phi_n|\hat{A}|\psi_j\rangle\langle\psi_j|\phi_n\rangle \\ &= \sum_n\sum_j p_j\langle\psi_j|\phi_n\rangle\langle\phi_n|\hat{A}|\psi_j\rangle \\ &= \sum_j p_j\langle\psi_j|\hat{A}|\psi_j\rangle = Tr\left\{\hat{\rho}\hat{A}\right\}, \end{aligned} \tag{10.53}$$

where the last equality results from Eq. (10.50). Also note that $Tr\left\{\hat{\rho}(t)\right\} = Tr\left\{\hat{\rho}\right\}$ for $\hat{\rho}(t)$ given by Eq. (10.45).

In addition to the fact that the diagonal elements of a density operator are always nonnegative, there are two important properties concerning traces of density operators as described below.

Traces of Density and Squared Density Operators

For any density operator, $\hat{\rho}$, the following two properties hold true.

$$Tr\left\{\hat{\rho}\right\} = 1, \tag{10.54}$$

$$0 \leq Tr\left\{\hat{\rho}^2\right\} \leq 1. \tag{10.55}$$

The proof of Eq. (10.54) is straightforward and results from that the sum of all the probabilities is equal to one as follows.

$$\begin{aligned} Tr\left\{\hat{\rho}\right\} &= \sum_n \langle\phi_n|\hat{\rho}|\phi_n\rangle = \sum_n \sum_j p_j \langle\phi_n|\psi_j\rangle\langle\psi_j|\phi_n\rangle \\ &= \sum_j p_j \langle\psi_j| \left(\sum_n |\phi_n\rangle\langle\phi_n|\right) |\psi_j\rangle = \sum_j p_j = 1, \end{aligned} \tag{10.56}$$

where the fact that $|\psi_j\rangle$'s are normalized and that $|\phi_n\rangle$'s form a complete basis has been used.

The proof of Eq. (10.55) is more involved but is straightforward as shown below.

$$\begin{aligned} Tr\left\{\hat{\rho}^2\right\} &= \sum_n \langle\phi_n|\hat{\rho}\hat{\rho}|\phi_n\rangle \\ &= \sum_n \sum_j \sum_k p_j p_k \langle\phi_n|\psi_j\rangle\langle\psi_j|\psi_k\rangle\langle\psi_k|\phi_n\rangle \\ &= \sum_j \sum_k p_j p_k \langle\psi_j|\psi_k\rangle \left(\sum_n \langle\psi_k|\phi_n\rangle\langle\phi_n|\psi_j\rangle\right) \\ &= \sum_j \sum_k p_j p_k \left|\langle\psi_j|\psi_k\rangle\right|^2 \leq \sum_j \sum_k p_j p_k = 1, \end{aligned} \tag{10.57}$$

where the fact that $\left|\langle\psi_j|\psi_k\rangle\right|^2 \leq 1$ has been used. Note that the equality is satisfied only for pure states. The above expression is obviously nonnegative since each term in the summation is nonnegative. This also proves the fact that $0 \leq Tr\left\{\hat{\rho}^2\right\}$.

The necessity to introduce a mixed state goes beyond any experimental imperfection, but has also more fundamental quantum mechanical origin. Mixed states can emerge for any system that cannot be completely decoupled from the rest of the universe even though there is no direct coupling of the system Hamiltonian and that of the rest [56]. For this, let us consider the direct product space of the system, for which $|\phi_n\rangle$'s form a complete basis, and the rest of the universe, for which we assume the existence of a complete orthonormal basis denoted as $|X_\gamma\rangle$'s. Since the entire universe is closed, any state defined in the direct product space can be expressed as the following linear combination:

$$|\Psi\rangle = \sum_n \sum_\gamma C_{n\gamma} |\phi_n\rangle \otimes |X_\gamma\rangle. \tag{10.58}$$

Let us assume that we are interested in calculating the expectation value of an operator $\hat{A}$, which is defined in the system space only. Then,

$$\begin{aligned}
\langle \hat{A} \rangle &= \sum_n \sum_{n'} \sum_\gamma \sum_{\gamma'} C^*_{n\gamma} C_{n'\gamma'} \langle \phi_n | \hat{A} | \phi_{n'} \rangle \langle X_\gamma | X_{\gamma'} \rangle \\
&= \sum_n \sum_{n'} \sum_\gamma C^*_{n\gamma} C_{n'\gamma} \langle \phi_n | \hat{A} | \phi_{n'} \rangle \\
&= \sum_n \sum_{n'} \left(\sum_\gamma C^*_{n\gamma} C_{n'\gamma} \right) \langle \phi_n | \hat{A} | \phi_{n'} \rangle,
\end{aligned} \tag{10.59}$$

where $\langle X_\gamma | X_{\gamma'} \rangle = \delta_{\gamma\gamma'}$ has been used in the second equality. The above average in general cannot be expressed in terms of a pure state defined as a linear combination of $|\phi_n\rangle$'s only. On the other hand, one can employ the following density operator:

$$\hat{\rho} = \sum_{n'} \sum_n \left(\sum_\gamma C^*_{n\gamma} C_{n'\gamma} \right) |\phi_{n'}\rangle \langle \phi_n|. \tag{10.60}$$

The above operator satisfies all the properties of a density operator. It is obvious that this operator is Hermitian and has nonnegative diagonal elements in any basis. The trace of this is equal to one as follows:

$$Tr\left\{\hat{\rho}\right\} = \sum_n \left(\sum_\gamma |C_{j\gamma}|^2 \right) = 1, \tag{10.61}$$

which is satisfied because $|\Psi\rangle$ given by Eq. (10.58) is normalized. On the other hand,

$$Tr\left\{\hat{\rho}^2\right\} = Tr\left\{\sum_{n'}\sum_{n}\sum_{n''}\left(\sum_{\gamma} C_{n\gamma}^* C_{n'\gamma}\right)\left(\sum_{\gamma'} C_{n''\gamma'}^* C_{n\gamma'}\right)|\phi_{n'}\rangle\langle\phi_{n''}|\right\}$$

$$= \sum_{n'}\sum_{n}\left|\sum_{\gamma} C_{n\gamma}^* C_{n'\gamma}\right|^2, \quad (10.62)$$

which can be shown to be always less than or equal to one.

Thus, $\hat{\rho}$ given by Eq. (10.60) in general represents a mixed state created due to an entanglement of the system with other environmental degrees freedom, for which no explicit control or specification through measurement is possible. On the other hand, it is straightforward to show that the average value given by Eq. (10.59) is indeed equal to $Tr\left\{\hat{A}\hat{\rho}\right\}$. In other words, the definition of average, Eq. (10.48), is general and can be used even when the average value cannot be expressed as an expectation value with respect to pure system states.

An important class of density operators is called the canonical equilibrium density operator, which is defined as follows:

$$\hat{\rho}_\beta = \frac{e^{-\beta\hat{H}}}{Z_\beta}, \quad (10.63)$$

where $\hat{H}$ is the Hamiltonian of the system, $\beta = 1/(k_B T)$, with k_B being the Boltzmann constant, and Z_β is the partition function of the canonical ensemble defined as

$$Z_\beta = Tr\{e^{-\beta\hat{H}}\} = \sum_j e^{-\beta E_j}. \quad (10.64)$$

In the above expression, E_j's are eigenvalues of the Hamiltonian $\hat{H}$. By definition, $Tr\{\hat{\rho}_\beta\} = 1$. In addition, it is stationary with respect to time since it commutes with the time evolution operator. For any physical observable, $\hat{A}$, the equilibrium average over the canonical ensemble is given by

$$\langle\hat{A}\rangle_\beta = Tr\left\{\hat{A}\hat{\rho}_\beta\right\}. \quad (10.65)$$

10.2.2 Time Dependent Perturbation Theory for Mixed Quantum States

Let us consider again the case where the total Hamiltonian $\hat{H}(t)$ is given by the sum of the zeroth order and time dependent first order terms such as Eq. (10.13), and denote the time evolution operator for this time dependent Hamiltonian as $\hat{U}_H(t)$. Given the density operator $\hat{\rho}(0)$ at time $t = 0$, the density operator at time t becomes

$$\hat{\rho}(t) = \hat{U}_H(t)\hat{\rho}(0)\hat{U}_H^\dagger(t). \tag{10.66}$$

On the other hand, the time dependent state at time t in the interaction picture with respect to $\hat{H}_0$ is

$$|\psi; t\rangle_I = \hat{U}_0^\dagger(t)|\psi; t\rangle = \hat{U}_0^\dagger(t)\hat{U}_H(t)|\psi; 0\rangle. \tag{10.67}$$

Let us combine this with Eq. (10.22) and note the fact that the initial state, $|\psi; 0\rangle = |\psi; 0\rangle_I$, is general. Therefore, we obtain the following identity:

$$\hat{U}_H(t) = \hat{U}_0(t)\exp_{(+)}\left[-\frac{i}{\hbar}\int_0^t dt'\hat{H}_{1,I}(t')\right], \tag{10.68}$$

where the second term in the above expression is a time-ordered exponential operator defined as

$$\begin{aligned}\exp_{(+)}\left[-\frac{i}{\hbar}\int_0^t dt'\hat{H}_{1,I}(t')\right] &\equiv \Bigg(1 - \frac{i}{\hbar}\int_0^t dt'\hat{H}_{1,I}(t') \\ &+ \left(-\frac{i}{\hbar}\right)^2 \int_0^t dt' \int_0^{t'} dt''\hat{H}_{1,I}(t')\hat{H}_{1,I}(t'') \\ &+ \left(-\frac{i}{\hbar}\right)^3 \int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} dt'''\hat{H}_{1,I}(t')\hat{H}_{1,I}(t'')\hat{H}_{1,I}(t''') + \cdots\Bigg).\end{aligned} \tag{10.69}$$

The subscript (+) in the above expression implies positive or chronological time ordering.

Employing the definition of $\hat{H}_{1,I}(t)$ given by Eq. (10.19) in Eq. (10.68), we obtain the following expression for the time evolution operator:

$$\begin{aligned}\hat{U}_H(t) = &e^{-i\hat{H}_0 t/\hbar} \\ &-\frac{i}{\hbar}\int_0^t dt' e^{-i\hat{H}_0(t-t')/\hbar}\hat{H}_1(t')e^{-i\hat{H}_0 t'/\hbar}\end{aligned}$$

$$+\left(-\frac{i}{\hbar}\right)^2 \int_0^t dt' \int_0^{t'} dt'' e^{-i\hat{H}_0(t-t')/\hbar} \hat{H}_1(t') e^{-i\hat{H}_0(t'-t'')/\hbar} \hat{H}_1(t'') e^{-i\hat{H}_0 t''/\hbar}$$
$$+\cdots . \tag{10.70}$$

Employing the above expression and its Hermitian conjugate in Eq. (10.66) and keeping only up to the second order terms with respect to $\hat{H}_1(t)$, we thus obtain the following second order approximation for the time dependent density operator:

$$\begin{aligned}
\hat{\rho}^{(2)}(t) = {} & e^{-i\hat{H}_0 t/\hbar} \hat{\rho}(0) e^{i\hat{H}_0 t/\hbar} \\
& -\frac{i}{\hbar} \int_0^t dt' e^{-i\hat{H}_0(t-t')/\hbar} \hat{H}_1(t') e^{-i\hat{H}_0 t'/\hbar} \hat{\rho}(0) e^{i\hat{H}_0 t/\hbar} \\
& +\frac{i}{\hbar} \int_0^t dt' e^{-i\hat{H}_0 t/\hbar} \hat{\rho}(0) e^{i\hat{H}_0 t'/\hbar} \hat{H}_1(t') e^{i\hat{H}_0(t-t')/\hbar} \\
& +\frac{1}{\hbar^2} \int_0^t dt' \int_0^t dt'' e^{-i\hat{H}_0(t-t')/\hbar} \hat{H}_1(t') e^{-i\hat{H}_0 t'/\hbar} \hat{\rho}(0) \\
& \qquad \times e^{i\hat{H}_0 t''/\hbar} \hat{H}_1(t'') e^{i\hat{H}_0(t-t'')/\hbar} \\
& -\frac{1}{\hbar^2} \int_0^t dt' \int_0^{t'} dt'' e^{-i\hat{H}_0(t-t')/\hbar} \hat{H}_1(t') e^{-i\hat{H}_0(t'-t'')/\hbar} \\
& \qquad \times \hat{H}_1(t'') e^{-i\hat{H}_0 t''/\hbar} \hat{\rho}(0) e^{i\hat{H}_0 t/\hbar} \\
& -\frac{1}{\hbar^2} \int_0^t dt' \int_0^{t'} dt'' e^{-i\hat{H}_0 t/\hbar} \hat{\rho}(0) e^{i\hat{H}_0 t''/\hbar} \hat{H}_1(t'') \\
& \qquad \times e^{i\hat{H}_0(t'-t'')/\hbar} \hat{H}_1(t') e^{i\hat{H}_0(t-t')/\hbar} .
\end{aligned} \tag{10.71}$$

For any physical observable $\hat{A}$, then its average value at time t including the effects of the perturbation up to the second order can be expressed as

$$\begin{aligned}
Tr\left\{\hat{A}\hat{\rho}^{(2)}(t)\right\} = {} & Tr\left\{e^{i\hat{H}_0 t/\hbar} \hat{A} e^{-i\hat{H}_0 t/\hbar} \hat{\rho}(0)\right\} \\
& -\frac{i}{\hbar} \int_0^t dt' Tr\left\{e^{i\hat{H}_0 t/\hbar} \hat{A} e^{-i\hat{H}_0(t-t')/\hbar} \hat{H}_1(t') e^{-i\hat{H}_0 t'/\hbar} \hat{\rho}(0)\right\} \\
& +\frac{i}{\hbar} \int_0^t dt' Tr\left\{e^{i\hat{H}_0 t'/\hbar} \hat{H}_1(t') e^{i\hat{H}_0(t-t')/\hbar} \hat{A} e^{-i\hat{H}_0 t/\hbar} \hat{\rho}(0)\right\} \\
& +\frac{1}{\hbar^2} \int_0^t dt' \int_0^t dt'' Tr\left\{e^{i\hat{H}_0 t''/\hbar} \hat{H}_1(t'') e^{i\hat{H}_0(t-t'')/\hbar} \hat{A} \right. \\
& \qquad \left. \times e^{-i\hat{H}_0(t-t')/\hbar} \hat{H}_1(t') e^{-i\hat{H}_0 t'/\hbar} \hat{\rho}(0)\right\}
\end{aligned}$$

$$
-\frac{1}{\hbar^2}\int_0^t dt' \int_0^{t'} dt'' Tr\left\{e^{i\hat{H}_0 t/\hbar}\hat{A}e^{-i\hat{H}_0(t-t')/\hbar}\hat{H}_1(t')\right.
\left. \times e^{-i\hat{H}_0(t'-t'')/\hbar}\hat{H}_1(t'')e^{-i\hat{H}_0 t''/\hbar}\hat{\rho}(0)\right\}
$$

$$
-\frac{1}{\hbar^2}\int_0^t dt' \int_0^{t'} dt'' Tr\left\{e^{i\hat{H}_0 t''/\hbar}\hat{H}_1(t'')e^{i\hat{H}_0(t'-t'')/\hbar}\hat{H}_1(t')\right.
\left. \times e^{i\hat{H}_0(t-t')/\hbar}\hat{A}e^{-i\hat{H}_0 t/\hbar}\hat{\rho}(0)\right\}, \tag{10.72}
$$

where we have used the identity, Eq. (10.50), repeatedly to send the density operator at time $t = 0$ to the rightmost place within the trace.

10.2.3 FGR for Mixed States

As an application of Eq. (10.72), let us consider a simple but widely used model. Assume that there is a two-state system spanned completely by $|1\rangle$ and $|2\rangle$, which form an orthonormal basis for the system. This system is coupled to all other degrees of freedom denoted as "bath." At the zeroth order level, this bath is independently coupled to each system state and does not couple them. Thus, the zeroth order Hamiltonian for the system plus bath is assumed to be

$$
\hat{H}_0 = (E_1 + \hat{B}_1)|1\rangle\langle 1| + (E_2 + \hat{B}_2)|2\rangle\langle 2| + \hat{H}_b, \tag{10.73}
$$

where $\hat{B}_1$ and $\hat{B}_2$ are bath operators representing the coupling of each state, $|1\rangle$ or $|2\rangle$, to the bath and $\hat{H}_b$ is the Hamiltonian for the bath only.

Examples of the two system states are spin states of any spin $1/2$ particle or two electronic states of interest in any molecular system. The total quantum state space is a direct product of the two system state space and that of the bath. Thus, the trace operation of an operator $\hat{O}$ that depends on both system and bath can be expressed as

$$
Tr\left\{\hat{O}\right\} = Tr_b\left\{\langle 1|\hat{O}|1\rangle + \langle 2|\hat{O}|2\rangle\right\}
= \langle 1|Tr_b\left\{\hat{O}\right\}|1\rangle + \langle 2|Tr_b\left\{\hat{O}\right\}|2\rangle. \tag{10.74}
$$

Let us assume that a small time dependent perturbation coupling the two system states is turned on at time $t = 0$. Thus, for $t \geq 0$,

$$
\hat{H}_1(t) = \hat{J}_{12}(t)|1\rangle\langle 2| + \hat{J}_{12}^{\dagger}(t)|2\rangle\langle 1|, \tag{10.75}
$$

where $\hat{J}(t)$ is time dependent (in general) and can also depend on the bath degrees of freedom. Thus, $\hat{J}(t)$ is assumed to be an operator in the bath space.

For $t \geq 0$, the total Hamiltonian becomes $\hat{H}(t) = \hat{H}_0 + \hat{H}_1(t)$. Let us assume that the total system plus the bath, before the perturbation Hamiltonian $\hat{H}_1(t)$ is turned on, is represented by the following density operator.

$$\hat{\rho}(0) = |1\rangle\langle 1|\hat{\rho}_b, \tag{10.76}$$

where $\hat{\rho}_b$ is a bath density operator that can be a canonical equilibrium density operator or any other nonequilibrium density operator. Thus, the above density operator represents the system prepared in the pure state $|1\rangle$ and the bath in some kind of mixed states as prescribed by $\hat{\rho}_b$.

Suppose that the major quantity of interest is the population of the state $|2\rangle$ of system at time t. This can be calculated, up to the second order of perturbation, by using $\hat{A} = |2\rangle\langle 2|$ in Eq. (10.72). Although there are many terms in Eq. (10.72), for the model and process considered here, most of the terms disappear because $\langle 2|e^{\pm i\hat{H}_0 t/\hbar}|1\rangle = \langle 1|e^{\pm i\hat{H}_0 t/\hbar}|2\rangle = 0$. Thus, Eq. (10.72) simplifies to

$$\begin{aligned} P_2^{(2)}(t) &= Tr\left\{|2\rangle\langle 2|\hat{\rho}^{(2)}(t)\right\} \\ &= \frac{1}{\hbar^2}\int_0^t dt'\int_0^t dt'' Tr\left\{e^{i\hat{H}_0 t''/\hbar}\hat{H}_1(t'')e^{i\hat{H}_0(t-t'')/\hbar}|2\rangle\langle 2|\right. \\ &\qquad\qquad \left.\times e^{-i\hat{H}_0(t-t')/\hbar}\hat{H}_1(t')e^{-i\hat{H}_0 t'/\hbar}\hat{\rho}(0)\right\} \\ &= \frac{1}{\hbar^2}\int_0^t dt'\int_0^t dt'' Tr_b\left\{\langle 1|e^{i\hat{H}_0 t''/\hbar}\hat{H}_1(t'')e^{i\hat{H}_0(t-t'')/\hbar}|2\rangle\right. \\ &\qquad\qquad \left.\times\langle 2|e^{-i\hat{H}_0(t-t')/\hbar}\hat{H}_1(t')e^{-i\hat{H}_0 t'/\hbar}|1\rangle\hat{\rho}_b\right\}. \end{aligned} \tag{10.77}$$

Since $\hat{H}_0$ given by Eq. (10.73) is diagonal with respect to the two state system states, it is easy to confirm that

$$e^{\pm i\hat{H}_0 t/\hbar} = e^{\pm i(E_1+\hat{B}_1+\hat{H}_B)t/\hbar}|1\rangle\langle 1| + e^{\pm i(E_2+\hat{B}_2+\hat{H}_B)t/\hbar}|2\rangle\langle 2|. \tag{10.78}$$

Thus, employing the above identity in all the expressions having $\hat{H}_0$ in the exponent in Eq. (10.77), we obtain

$$\begin{aligned} P_2^{(2)}(t) = \frac{1}{\hbar^2}\int_0^t dt'\int_0^t dt'' Tr_b&\left\{e^{i(E_1+\hat{B}_1+\hat{H}_b)t''/\hbar}\langle 1|\hat{H}_1(t'')|2\rangle e^{i(E_2+\hat{B}_2+\hat{H}_b)(t-t'')/\hbar}\right. \\ &\left.\times e^{-i(E_2+\hat{B}_2+\hat{H}_b)(t-t')/\hbar}\langle 2|\hat{H}_1(t')|1\rangle e^{-i(E_1+\hat{B}_1+\hat{H}_b)t'/\hbar}\hat{\rho}_b\right\} \end{aligned}$$

$$= \frac{1}{\hbar^2} \int_0^t dt' \int_0^t dt'' e^{i(E_2 - E_1)(t' - t'')/\hbar} Tr_b \left\{ e^{i(\hat{B}_1 + \hat{H}_b)t''/\hbar} \hat{J}_{12}(t'') \right.$$
$$\left. \times e^{i(\hat{B}_2 + \hat{H}_b)(t' - t'')/\hbar} \hat{J}_{12}^{\dagger}(t') e^{-i(\hat{B}_1 + \hat{H}_b)t'/\hbar} \hat{\rho}_b \right\}. \tag{10.79}$$

The second equality of the above expression is obtained by further rearrangement of terms and using the definition of $\hat{H}_1(t)$ given by Eq. (10.75) explicitly.

Now let us define the transition rate from state 1 to state 2 as the time derivative of $P_2^{(2)}(t)$. Then,

$$\Gamma_{1\to 2}(t) = \frac{d}{dt} P_2^{(2)}(t)$$
$$= \frac{1}{\hbar^2} \int_0^t dt'' \; e^{i(E_2 - E_1)(t - t'')/\hbar} Tr_b \left\{ e^{i(\hat{B}_1 + \hat{H}_b)t''/\hbar} \hat{J}_{12}(t'') \right.$$
$$\left. \times e^{i(\hat{B}_2 + \hat{H}_b)(t - t'')/\hbar} \hat{J}_{12}^{\dagger}(t) e^{-i(\hat{B}_1 + \hat{H}_b)t/\hbar} \hat{\rho}_b \right\}$$
$$+ \frac{1}{\hbar^2} \int_0^t dt' \; e^{i(E_2 - E_1)(t' - t)/\hbar} Tr_b \left\{ e^{i(\hat{B}_1 + \hat{H}_b)t/\hbar} \hat{J}_{12}(t) \right.$$
$$\left. \times e^{i(\hat{B}_2 + \hat{H}_b)(t' - t)/\hbar} \hat{J}_{12}^{\dagger}(t') e^{-i(\hat{B}_1 + \hat{H}_b)t'/\hbar} \hat{\rho}_b \right\}. \tag{10.80}$$

Replacing the integrands $t - t''$ and $t - t'$ to τ respectively and noting the fact that the two integrations above are complex conjugates of each other, we obtain the following general expression:

$$\Gamma_{1\to 2}(t) = \frac{2}{\hbar^2} \mathrm{Re} \left[\int_0^t d\tau \; e^{i(E_2 - E_1)\tau/\hbar} Tr_b \left\{ e^{i(\hat{B}_1 + \hat{H}_b)(t - \tau)/\hbar} \hat{J}_{12}(t - \tau) \right. \right.$$
$$\left. \left. \times e^{i(\hat{B}_2 + \hat{H}_b)\tau/\hbar} \hat{J}_{12}^{\dagger}(t) e^{-i(\hat{B}_1 + \hat{H}_b)t/\hbar} \hat{\rho}_b \right\} \right]. \tag{10.81}$$

The rate expression given above is valid for any time and any form of $\hat{J}(t)$ as long as these are small enough to justify the application of the first order time dependent perturbation theory. Thus, this can be used as the starting point for calculating rates under various physical conditions.

First, let us assume that

$$\hat{J}_{12}(t) = \hat{J}_{12} e^{i\omega t}, \tag{10.82}$$

where $\hat{J}_{12}$ is time independent but is still assumed to be an operator in the bath space. In addition, let us also assume that the bath density operator is the canonical

equilibrium density operator corresponding to the system state 1 as follows:

$$\hat{\rho}_{b,1}^{eq} = \frac{e^{-\beta(\hat{B}_1+\hat{H}_b)}}{Tr_b\left\{e^{-\beta(\hat{B}_1+\hat{H}_b)}\right\}}, \tag{10.83}$$

where $\beta = 1/(k_B T)$. Then, Eq. (10.81) simplifies further to

$$\Gamma_{1\to 2}(t) = \frac{2}{\hbar^2}\text{Re}\left[\int_0^t d\tau\ e^{i(E_2-E_1-\omega)\tau/\hbar} \times Tr_b\left\{e^{-i(\hat{B}_1+\hat{H}_b)\tau/\hbar}\hat{J}_{12}e^{i(\hat{B}_2+\hat{H}_b)\tau/\hbar}\hat{J}_{12}^{\dagger}\hat{\rho}_{b,1}^{eq}\right\}\right]. \tag{10.84}$$

Taking the limit of $t \to \infty$, the above rate becomes the following time independent rate expression:

$$\Gamma_{1\to 2}^{s} = \frac{2}{\hbar^2}\text{Re}\left[\int_0^\infty dt\ e^{i(E_2-E_1-\omega)t/\hbar}Tr_b\left\{e^{-i(\hat{B}_1+\hat{H}_b)t/\hbar}\hat{J}_{12}e^{i(\hat{B}_2+\hat{H}_b)t/\hbar}\hat{J}_{12}^{\dagger}\hat{\rho}_{b,1}^{eq}\right\}\right], \tag{10.85}$$

where we have replaced the integration variable τ with t.

Equation (10.85) is in fact a kind of the FGR rate expression. For the case where the perturbation Hamiltonian corresponds to the interaction of two states of a molecule with an electric field component of light and the Condon approximation holds, $\hat{J}_{12} = \mathcal{A}\boldsymbol{D}_{12}\cdot\mathbf{u}_e$, where $\boldsymbol{D}_{12}$ is the corresponding transition dipole vector. Equation (10.85) in this case reduces to the following lineshape expression for the transition from state 1 to state 2:

$$I_{1\to 2}^{s}(\omega) = \frac{|\mathcal{A}|^2|\boldsymbol{D}_{12}\cdot\mathbf{u}_e|^2}{\hbar^2} \times \int_{-\infty}^{\infty} dt\ e^{i(E_2-E_1-\omega)t/\hbar}Tr_b\left\{e^{i(\hat{B}_2+\hat{H}_b)t/\hbar}e^{-i(\hat{B}_1+\hat{H}_b)t/\hbar}\hat{\rho}_{b,1}^{eq}\right\}, \tag{10.86}$$

where we have used the fact that $\rho_{b,1}^{eq}$ commutes with $\hat{H}_b + \hat{B}_1$ and also made the dependence of the rate on ω explicit. For the case of absorption ($E_2 > E_1$), ω is positive. For the case of emission ($E_2 < E_1$), ω is negative, which represents emission of photon with frequency $-\omega$. Equation (10.86) can be used for the modeling of absorption and emission lineshapes of various electronic transitions and is reliable as long as the two states involved in the transition are well separated from others and assumptions of the model Hamiltonian are well justified.

Similarly, for the case where $\omega = 0$ and $\hat{J}_{12}$ is not a vector but a time independent constant, *i.e.*, J_{12}, Eq. (10.85) reduces to the following familiar FGR rate expression:

$$\Gamma_{FGR}^{1\rightarrow 2} = \frac{J_{12}^2}{\hbar^2} \int_{-\infty}^{\infty} dt\, e^{i(E_2-E_1)t/\hbar} Tr_b \left\{ e^{i(\hat{B}_2+\hat{H}_b)t/\hbar} e^{-i(\hat{B}_1+\hat{H}_b)t/\hbar} \hat{\rho}_{b,1}^{eq} \right\}. \tag{10.87}$$

Various rate processes involving transitions of quantum states such as the transfer of electron, excitation energy, or proton can be described in terms of the above FGR rate expression. Indeed, well known Marcus rate [33, 34] expression for the electron transfer rate or the Förster rate [35] expression for excitation energy transfer can be derived [36, 37] from this FGR expression with further approximations and consideration of relevant physical conditions.

10.3 Summary and Questions

In the Schrödinger picture, the dynamics of a quantum system can be viewed as that due to the time evolution of states. On the other hand, physical observables are represented by time dependent operators unless explicit time dependence is needed due to external factors. In the Heisenberg picture, the view is opposite and the time dependence is carried through that of time dependent Heisenberg operators defined by Eq. (10.5). Interaction picture is in-between the two pictures and assumes that the operators evolve according to a zeroth or reference Hamiltonian while the states evolve according to the remaining part that represents the key interaction term of the Hamiltonian that is the major focus of the dynamics study. All of these pictures are equivalent because of the unitarity of a time evolution operator.

Time dependent perturbation theory allows calculation of the effects of a perturbation Hamiltonian on the time evolution of states and physical observables and can be best expressed in the interaction picture where the state evolves in time only due to the perturbation Hamiltonian term. Considering only the first order term, one obtains a simple and general expression for the state in the interaction picture, Eq. (10.23), and that in the Schrödinger picture, Eq. (10.24). Use of this expression for the calculation of the transition probability between two states and calculation of the transition rate as its time derivative in the stead state limit leads to the FGR rate expression. This leads to the well-known expression for the intensity of spectroscopic transition, Eq. (10.34). For the case of transitions to a collection of final states with energy density $\rho_f(E)$, averaging of the FGR rate expression, Eq. (10.35), leads to the final rate expression, Eq. (10.38).

A broad class of physical systems requires introduction of mixed states that cannot be represented by a single ket (bra). This is because the system under study is a collection or ensemble of states due to experimental limitations in creating pure quantum states. More fundamentally, this can be due to the entanglement of the system under study with other environmental degrees of freedom. This requires introduction of a density operator, which can be expressed in general as Eq. (10.44),

for which time evolution in both ket and bra space becomes necessary. The resulting time evolution equation, Eq. (10.46), is known as quantum Liouville equation. The average of any physical observable for the density operator is given by Eq. (10.48), and any density operator is Hermitian and satisfies Eqs. (10.54) and (10.55).

Time dependent perturbation theory can be extended to the time evolution of the density operator by employing perturbation expansions for both time dependent kets and bras constituting the density operator. The resulting lowest order terms representing transitions between states now become second order with respect to the perturbation. Calculation of the time derivative of the probability for the system to be in a certain final state of interest and consideration of its steady state limit, results in a general expression for the FGR rate, Eq. (10.85). This expression is valid for a general mixed state given by Eq. (10.76) as the initial condition. The lineshape expression, Eq. (10.86), and a well-known FGR rate expression, Eq. (10.87), can then be obtained with additional assumptions and approximations.

Questions

- What are major differences between Schrödinger and Heisenberg pictures and why are the two pictures equivalent in describing quantum dynamics?
- What makes consideration in the interaction picture useful?
- Can one apply the time dependent perturbation theory even when the perturbation is time independent?
- What is the consequence of applying the time dependent perturbation theory when the initial states are degenerate?
- What are conditions and assumptions validating the use of the first order perturbation theory?
- Is the Fermi's golden rule rate always well defined and finite?
- Does an ensemble of quantum states always require description at the level of a density operator?
- What are physical origins of mixed states?
- What is the Condon approximation in lineshape calculation? What is its utility and what happens if the approximation breaks down?

Appendix: Interaction Hamiltonian in the Presence of Radiation

This section provides a brief overview of the classical theory of electromagnetic fields [38] and then outlines how the interaction between molecules and the classical radiation field can be treated. Thus, the approach being described here is semiclassical because only molecules are considered quantum mechanically

while the electromagnetic field is simply viewed as time dependent classical external potential. This approach is valid and practical for the description of simple spectroscopic experiments.

Classically, the Hamiltonian for a particle with mass m and charge q and its interaction with electric and magnetic fields, $\mathbf{E}(\mathbf{r}, \mathbf{t})$ and $\mathbf{B}(\mathbf{r}, t)$, in Gaussian units, can be expressed as [37, 38]

$$H = \frac{1}{2m}\left(\mathbf{p} - \frac{q}{c}\mathbf{A}(\mathbf{r}, t)\right)^2 + q\Phi(\mathbf{r}, t) + V(\mathbf{r}), \tag{10.88}$$

where $V(\mathbf{r})$ is the potential applied to the particle in the absence of the electromagnetic radiation and $\mathbf{A}(\mathbf{r}, t)$ and $\Phi(\mathbf{r}, t)$ are vector and scalar potentials that are related to the electric and magnetic fields, $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{B}(\mathbf{r}, t)$, as follows:

$$\mathbf{E}(\mathbf{r}, t) + \frac{1}{c}\frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t} = -\nabla\Phi(\mathbf{r}, t). \tag{10.89}$$

$$\mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t). \tag{10.90}$$

It is straightforward to show through vector calculus that Eq. (10.88) results in the following equation of motion [37, 38]:

$$m\frac{d^2\mathbf{r}}{dt^2} = q\left\{-\frac{1}{c}\frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t} - \nabla\Phi(\mathbf{r}, t)\right\} + \frac{q}{c}\frac{d\mathbf{r}}{dt} \times \{\nabla \times \mathbf{A}(\mathbf{r}, t)\} - \nabla V(\mathbf{r}). \tag{10.91}$$

Inserting Eqs. (10.89) and (10.90) into the above equation, one can show that it is equivalent to the following equation of motion that is more well-known:

$$m\frac{d^2\mathbf{r}}{dt^2} = q\left(\mathbf{E}(\mathbf{r}, t) + \frac{1}{c}\frac{d\mathbf{r}}{dt} \times \mathbf{B}(\mathbf{r}, t)\right) - \nabla V(\mathbf{r}) . \tag{10.92}$$

The definitions of electric and magnetic fields, Eqs. (10.89) and (10.90), leave great degree of flexibility in choosing the vector and scalar potentials because, for an arbitrary function $f(\mathbf{r}, t)$, the following replacement does not cause any difference in the electric and magnetic fields.

$$\mathbf{A}'(\mathbf{r}, t) = \mathbf{A}(\mathbf{r}, t) + \nabla f(\mathbf{r}, t), \tag{10.93}$$

$$\Phi'(\mathbf{r}, t) = \Phi(\mathbf{r}, t) - \frac{1}{c}\frac{\partial f(\mathbf{r}, t)}{\partial t}. \tag{10.94}$$

In other words,

$$\mathbf{B}(\mathbf{r},t) = \nabla \times \mathbf{A}'(\mathbf{r},t), \tag{10.95}$$

$$\mathbf{E}(\mathbf{r},t) + \frac{1}{c}\frac{\partial \mathbf{A}'(\mathbf{r},t)}{\partial t} = -\nabla \Phi'(\mathbf{r},t). \tag{10.96}$$

Equations (10.93) and (10.94) are called gauge transformation, and provide ways to choose appropriate vector and scalar potentials that are easy to work with while not changing the electric and magnetic fields. One important gauge is called **Coulomb gauge**, which is characterized by the following condition:

$$\nabla \cdot \mathbf{A}(\mathbf{r},t) = 0. \tag{10.97}$$

The gauge transformation, Eqs. (10.93) and (10.94), makes it always possible to find a vector potential satisfying the above property. Let us assume that we happen to know a pair of $\mathbf{A}'$ and Φ' corresponding to given electric and magnetic fields, but that $\nabla \cdot \mathbf{A}' \neq 0$. Then, we can choose a function f in Eq. (10.93) such that $\nabla \cdot \mathbf{A}' = \nabla^2 f$. The resulting $\mathbf{A}$ satisfies the Coulomb gauge condition, Eq. (10.97).

In a continuous medium satisfying linear constitutive relations with dielectric constant ϵ and magnetic permeability μ, Maxwell's equations can be shown to be equivalent to the following partial differential equations for the vector and scalar potentials:

$$-\frac{1}{c}\frac{\partial}{\partial t}\left(\nabla \cdot \mathbf{A}(\mathbf{r},t)\right) - \nabla^2 \Phi(\mathbf{r},t) = \frac{4\pi\rho(\mathbf{r},t)}{\epsilon}, \tag{10.98}$$

$$\nabla\left(\nabla \cdot \mathbf{A}(\mathbf{r},t)\right) - \nabla^2 \mathbf{A}(\mathbf{r},t) - \frac{\epsilon\mu}{c}\frac{\partial}{\partial t}\left(-\frac{1}{c}\frac{\partial \mathbf{A}(\mathbf{r},t)}{\partial t} - \nabla \Phi(\mathbf{r},t)\right) = \frac{4\pi\mu}{c}\mathbf{J}(\mathbf{r},t), \tag{10.99}$$

where $\rho(\mathbf{r},t)$ and $\mathbf{J}(\mathbf{r},t)$ are charge and current densities. In Coulomb gauge where Eq. (10.97) is satisfied, the above equations are simplified further to

$$-\nabla^2 \Phi(\mathbf{r},t) = \frac{4\pi\rho(\mathbf{r},t)}{\epsilon}, \tag{10.100}$$

$$-\nabla^2 \mathbf{A}(\mathbf{r},t) + \frac{\epsilon\mu}{c^2}\frac{\partial^2 \mathbf{A}(\mathbf{r},t)}{\partial t^2} + \frac{\epsilon\mu}{c}\frac{\partial}{\partial t}\nabla \Phi(\mathbf{r},t) = \frac{4\pi\mu}{c}\mathbf{J}(\mathbf{r},t). \tag{10.101}$$

Let us now consider the simplest case where there are no sources of charge and current. Then, $\rho(\mathbf{r},t) = 0$ and $\mathbf{J}(\mathbf{r},t) = 0$, and Eq. (10.100) reduces to

$$\nabla^2 \Phi(\mathbf{r},t) = 0. \tag{10.102}$$

A solution of this, which satisfies the boundary condition of the infinite space, is that $\Phi = 0$. That is, in free space, the scalar potential can be assumed to be zero (in the Coulomb gauge). With this assumption, Eq. (10.101) now simplifies to

$$\nabla^2 \mathbf{A}(\mathbf{r}, t) - \frac{\epsilon\mu}{c^2}\frac{\partial^2 \mathbf{A}(\mathbf{r}, t)}{\partial t^2} = 0. \tag{10.103}$$

Many solutions are possible for this partial differential equation. One of the simplest solutions is the following plane wave solution:

$$\mathbf{A}(\mathbf{r}, t) = A_0 \mathbf{u}_e \cos(\mathbf{k} \cdot \mathbf{r} - \omega t), \tag{10.104}$$

where

$$k^2 = |\mathbf{k}|^2 = \frac{\epsilon\mu}{c^2}\omega^2, \tag{10.105}$$

Assuming that both ϵ and μ are real and positive (non-absorptive medium), the refractive index is defined as

$$n = \sqrt{\epsilon\mu}. \tag{10.106}$$

Thus, in a medium with refractive index n, the plane wave solution travels with a speed $v = \omega/k = c/n$.

Inserting Eq. (10.104) into the condition Eq. (10.97), one can find that

$$\mathbf{k} \cdot \mathbf{u}_e = 0. \tag{10.107}$$

That is, $\mathbf{u}_e$ is perpendicular to the direction of the propagation of the vector potential. Inserting Eq. (10.104) into Eq. (10.90),

$$\mathbf{B}(\mathbf{r}, t) = A_0(\mathbf{k} \times \mathbf{u}_e) \sin(\omega t - \mathbf{k} \cdot \mathbf{r}) = A_0 k \mathbf{u}_b \sin(\omega t - \mathbf{k} \cdot \mathbf{r}), \tag{10.108}$$

where $\mathbf{u}_b = \mathbf{k} \times \mathbf{u}_e/k$, the direction of the magnetic field. Inserting Eq. (10.104) into Eq. (10.96) with $\Phi = 0$,

$$\mathbf{E} = \frac{A_0\omega}{c}\mathbf{u}_e \sin(\omega t - \mathbf{k} \cdot \mathbf{r}) = \frac{A_0 k}{n}\mathbf{u}_e \sin(\omega t - \mathbf{k} \cdot \mathbf{r}). \tag{10.109}$$

For the case of a a quantum mechanical particle with mass m and charge q in the presence of an electromagnetic field, which is still treated as a classical wave, the Hamiltonian operator is obtained by simply replacing the physical observables in Eq. (10.88) with quantum operators as follows:

$$\hat{H} = \frac{1}{2m}\left(\hat{\mathbf{p}} - \frac{q}{c}\mathbf{A}(\hat{\mathbf{r}}, t)\right)^2 + q\Phi(\hat{\mathbf{r}}, t) + V(\hat{\mathbf{r}}), \tag{10.110}$$

where $\hat{\mathbf{p}}$ and $\hat{\mathbf{r}}$ are momentum and position operators. Expanding the square in Eq. (10.110),

$$\left(\hat{\mathbf{p}} - \frac{q}{c}\mathbf{A}(\hat{\mathbf{r}}, t)\right)^2 = \hat{\mathbf{p}}^2 - \frac{q}{c}\hat{\mathbf{p}} \cdot \mathbf{A}(\hat{\mathbf{r}}, t) - \frac{q}{c}\mathbf{A}(\hat{\mathbf{r}}, t) \cdot \hat{\mathbf{p}} + \frac{q^2}{c^2}\mathbf{A}(\hat{\mathbf{r}}, t)^2. \tag{10.111}$$

Employing the following identity:

$$\hat{\mathbf{p}} \cdot \mathbf{A}(\hat{\mathbf{r}}, t) = \mathbf{A}(\hat{\mathbf{r}}, t) \cdot \hat{\mathbf{p}} + \frac{\hbar}{i}\nabla \cdot \mathbf{A}(\hat{\mathbf{r}}, t), \tag{10.112}$$

the Hamiltonian of Eq. (10.110) can be expressed as

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{r}}) + q\Phi(\hat{\mathbf{r}}, t) - \frac{q}{mc}\mathbf{A}(\hat{\mathbf{r}}, t) \cdot \hat{\mathbf{p}} - \frac{\hbar q}{ic}\nabla \cdot \mathbf{A}(\hat{\mathbf{r}}, t) + \frac{q^2}{2mc^2}\mathbf{A}(\hat{\mathbf{r}}, t)^2 . \tag{10.113}$$

In Coulomb gauge, $\nabla \cdot \mathbf{A}(\hat{\mathbf{r}}, t) = 0$. In addition, assuming weak enough field, the quadratic term $\mathbf{A}(\hat{\mathbf{r}}, t)^2$ can be neglected. As a result, Eq. (10.110) can be approximated as

$$\hat{H}(t) = \hat{H}_0 + q\Phi(\hat{\mathbf{r}}, t) - \frac{q}{mc}\mathbf{A}(\hat{\mathbf{r}}, t) \cdot \hat{\mathbf{p}}, \tag{10.114}$$

where $\hat{H}_0$ is the Hamiltonian in the absence of the electromagnetic radiation and is given by

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{r}}) . \tag{10.115}$$

Let us consider the case where the particle is subject to a monochromatic radiation of frequency ω. Then, using the fact $\Phi(\hat{\mathbf{r}}, t) = 0$ and inserting Eq. (10.104) into Eq. (10.114), we find the following time dependent Hamiltonian:

$$\hat{H}(t) = \hat{H}_0 + \hat{H}_1(t), \tag{10.116}$$

where

$$\hat{H}_1(t) = -\frac{q}{2mc}A_0\left(e^{i\mathbf{k}\cdot\hat{\mathbf{r}}-i\omega t} + e^{-i\mathbf{k}\cdot\hat{\mathbf{r}}+i\omega t}\right)\mathbf{u}_e \cdot \hat{\mathbf{p}}. \tag{10.117}$$

In a typical molecular spectroscopy, the wavelength of the radiation is much larger than the molecular length scale. Therefore, one can make an approximation that $\mathbf{k} \cdot \hat{\mathbf{r}} \approx 0$, which is referred to as *dipole approximation* for a reason to be clear below. Then, the matter radiation interaction can be approximated as

$$\hat{H}_1(t) \approx -\frac{q}{2mc} A_0 \left(e^{-i\omega t} + e^{i\omega t} \right) \mathbf{u}_e \cdot \hat{\mathbf{p}}, \tag{10.118}$$

where the momentum operator $\hat{\mathbf{p}}$ can be expressed in terms of the position operator employing the following relation:

$$\hat{\mathbf{p}} = \frac{im}{\hbar} \left[\hat{H}_0, \hat{\mathbf{r}} \right]. \tag{10.119}$$

Then, Eq. (10.118) can be expressed as

$$\hat{H}_1(t) = -\frac{i}{2\hbar c} A_0 \left(e^{-i\omega t} + e^{i\omega t} \right) \left[H_0, \mathbf{u}_e \cdot \hat{\boldsymbol{D}} \right], \tag{10.120}$$

where $\hat{\boldsymbol{D}} = q\hat{\mathbf{r}}$, the dipole operator. That is, the radiation interacts with the dipole operator and this is the reason why the approximation of $\mathbf{k} \cdot \hat{\mathbf{r}} \approx 0$ is called dipole approximation.

Let us consider the matrix element of $\hat{H}_1(t)$ between two orthonormal eigenstates of $\hat{H}_0$ with eigenvalues E_j and E_k as follows:

$$\begin{aligned} \langle E_j | \hat{H}_1(t) | E_k \rangle &= -\frac{i}{2\hbar c} A_0 \left(e^{-i\omega t} + e^{i\omega t} \right) \langle E_j | \left[H_0, \mathbf{u}_e \cdot \hat{\boldsymbol{D}} \right] | E_k \rangle \\ &= -\frac{i}{2\hbar c} A_0 \left(e^{-i\omega t} + e^{i\omega t} \right) (E_j - E_k) \langle E_j | \mathbf{u}_e \cdot \hat{\boldsymbol{D}} | E_k \rangle \\ &= -\frac{i}{2\hbar c} A_0 \left(e^{-i\omega t} + e^{i\omega t} \right) (E_j - E_k) \mathbf{u}_e \cdot \boldsymbol{D}_{jk}, \end{aligned} \tag{10.121}$$

where $\boldsymbol{D}_{jk}$ is the transition dipole vector between states $|E_j\rangle$ and $|E_k\rangle$. The above expression has two time dependent terms, one of which becomes almost non-oscillatory when resonant with the energy difference between the final and initial states. On the other hand, the other becomes highly oscillatory. Ignoring this highly oscillatory term and keeping only the resonant term is called *rotating wave approximation*.

All the expressions derived above can easily be extended to molecular or many particle systems, and the resulting expressions similar to Eq. (10.121), along with the rotating wave approximation, leads to the interaction Hamiltonian such as Eq. (10.33).

The description of molecule-radiation interaction presented here is limited to linear interactions and semiclassical in nature since the electromagnetic wave is treated classically. There are well-established theories of higher order molecule-radiation interactions [39, 40] or fully quantum mechanical treatment of radiation [20, 41], which can provide more modern perspective of molecule-radiation interactions.

Exercise Problems with Solutions

10.1 A one dimensional harmonic oscillator with mass m and angular frequency ω is subject to the following time dependent perturbation Hamiltonian:

$$\hat{H}_1(t) = Ae^{-t/\tau}(\hat{b} + \hat{b}^\dagger), \text{ for } t > 0$$

where τ and A are positive real numbers, and $\hat{b}$ and $\hat{b}^\dagger$ are lowering and raising operators of the harmonic oscillator corresponding to the zeroth order Hamiltonian $\hat{H}_0$. Given that the state at time $t = 0$ is $|j\rangle$, the eigenstate of the zeroth order Hamiltonian with eigenvalue $E_j = \hbar\omega(j + \frac{1}{2})$, the first order time dependent perturbation theory approximation for the state at time t is

$$|\psi; t\rangle^{(1)} = e^{-\frac{i}{\hbar}E_j t}|j\rangle - \frac{i}{\hbar}\int_0^t dt' e^{-\frac{i}{\hbar}\hat{H}_0(t-t')}\hat{H}_1(t')e^{-\frac{i}{\hbar}E_j t'}|j\rangle.$$

Assume that $j = 1$. Then, calculate the probability for the state to be at $|2\rangle$ at time $t = \pi/\omega$.

Solution 10.1

$$\langle 2|\psi; t\rangle = -\frac{i}{\hbar}\int_0^t dt' e^{-\frac{i}{\hbar}E_2(t-t')}Ae^{-t'/\tau}\langle 2|(\hat{b} + \hat{b}^\dagger)|1\rangle e^{-\frac{i}{\hbar}E_1 t'}$$

$$= -\frac{i}{\hbar}A\sqrt{2}e^{-\frac{i}{\hbar}E_2 t}\int_0^t dt' e^{-(\frac{1}{\tau}-i\omega)t'} = -\frac{i}{\hbar}A\sqrt{2}e^{-\frac{i}{\hbar}E_2 t}\frac{1 - e^{-(\frac{1}{\tau}-i\omega)t}}{\frac{1}{\tau} - i\omega}.$$

$$\text{Probability: } |\langle 2|\psi; t = \pi/\omega\rangle|^2 = \frac{2|A|^2}{\hbar^2}\frac{(1 + e^{-\pi/(\omega\tau)})^2}{(1/\tau)^2 + \omega^2}.$$

10.2 Consider the following operator

$$\hat{\rho} = \begin{pmatrix} \frac{1}{4} & 0 & C \\ 0 & \frac{1}{4} & 0 \\ C & 0 & \frac{1}{2} \end{pmatrix},$$

where C is a real number. Find out the largest possible value of C for $\hat{\rho}$ to be a density operator.

Solution 10.2

$$\hat{\rho}^2 = \begin{pmatrix} \frac{1}{4} & 0 & C \\ 0 & \frac{1}{4} & 0 \\ C & 0 & \frac{1}{2} \end{pmatrix}\begin{pmatrix} \frac{1}{4} & 0 & C \\ 0 & \frac{1}{4} & 0 \\ C & 0 & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} \frac{1}{16} + C^2 & 0 & \frac{3C}{4} \\ 0 & \frac{1}{16} & 0 \\ \frac{3C}{4} & 0 & \frac{1}{4} + C^2 \end{pmatrix}.$$

Since $Tr\{\hat{\rho}^2\} \leq 1$, $\frac{3}{8} + 2C^2 \leq 1$. Therefore, $C^2 \leq \frac{5}{16}$. As a result, the largest possible value of C is $\sqrt{5}/4$.

Problems

10.3 Prove the following identity.

$$\frac{i}{\hbar}[\hat{p}, \hat{V}(\hat{x})] = \hat{V}'(\hat{x}),$$

where $V'(x)$ is the derivative of $V(x)$.

10.4 For a harmonic oscillator with mass m and angular frequency ω, its lowering and raising operators are defined by Eqs. (3.51) and (3.52). Prove that their Heisenberg operators are expressed as $\hat{b}_H(t) = \hat{b}e^{-i\omega t}$ and $\hat{b}_H^\dagger(t) = \hat{b}^\dagger e^{i\omega t}$.

10.5 Calculate the average energy, square displacement, and kinetic energy for a canonical ensemble of harmonic oscillators and examine how they depend on temperature.

10.6 A one dimensional harmonic oscillator with mass m and angular frequency ω is subject to the following time dependent perturbation Hamiltonian:

$$\hat{H}_1(t) = Ae^{-t/\tau}(1 + \epsilon\hat{x}), \text{ for } t > 0,$$

where τ, A, and ϵ are positive real numbers, and $\hat{x}$ is the displacement of the harmonic oscillator. Let us denote the eigenstate of the zeroth order Hamiltonian, *i,e,*, the harmonic oscillator Hamiltonian, with energy $\hbar\omega(n+1/2)$ as $|n\rangle$. Given that the state at time $t = 0$ is $|\psi; 0\rangle = |1\rangle$ and assuming that A and ϵ are small enough, use the first order time dependent perturbation theory to answer the following questions.

(a) Find the expression for the first order time dependent perturbation approximation at time t, $|\psi; t\rangle^{(1)}$ (Hint: Express $\hat{x}$ in terms of raising and lowering operators $\hat{b}$ and $\hat{b}^\dagger$. Do the integration explicitly.)
(b) What is the probability for the oscillator to be in the state $|2\rangle$ at time $t = 1/\omega$?

10.7 Prove that $Tr\left\{\hat{\rho}^2\right\}$ given by Eq. (10.62) satisfies Eq. (10.55) using the Cauchy-Schwarz inequality.

10.8 For a system where two orthonormal states $|1\rangle$ and $|2\rangle$, a state is represented by the following density operator:

$$\hat{\rho} = \frac{1}{2}|1\rangle\langle 1| + \frac{1}{2}|2\rangle\langle 2| + C|1\rangle\langle 2| + C^*|2\rangle\langle 1|.$$

(a) Find the exact condition for C in order for the above operator is a genuine density operator.
(b) Find the exact condition for C in order for the above density operator to represent a pure state.

Chapter 11
Theories for Electronic Structure Calculation of Polyatomic Molecules



It is a profound and necessary truth that the deep things in science are not found because they are useful; they are found because it was possible to find them.

– J. Robert Oppenheimer

Abstract This chapter presents more detailed theoretical account of methods used for the calculation of electronic states of polyatomic molecules. The main focus is the Hartree-Fock (HF) approximation and its implementation employing finite basis as formulated by Roothaan. Brief accounts of more advanced methods that go beyond the HF approximation are provided. The basic principles underlying the Density Functional Theory (DFT) for the calculation of the ground electronic state of adiabatic electronic states are also explained.

In this chapter, we will go through in more detail how to find approximate solutions for the electronic Schrödinger equation, Eq. (9.9), or its equivalent. For this, let us rewrite the electronic Hamiltonian $\hat{H}_{el}$ given by Eq. (9.8) as follows:

$$\hat{H}_{el} = \sum_{\mu=1}^{N_e} \hat{h}_\mu + \frac{1}{2}\sum_{\mu=1}^{N_e}\sum_{\nu\neq\mu}\frac{1}{\hat{r}_{\mu\nu}}, \tag{11.1}$$

where

$$\hat{h}_\mu = \frac{\hat{\mathbf{p}}_\mu^2}{2} - \sum_{c=1}^{N_u}\frac{Z_c}{|\hat{\mathbf{r}}_\mu - \mathbf{R}_c|}, \tag{11.2}$$

$$\frac{1}{\hat{r}_{\mu\nu}} = \frac{1}{|\hat{\mathbf{r}}_\mu - \hat{\mathbf{r}}_\nu|}. \tag{11.3}$$

In above expressions, the parametric dependences of $\hat{h}_\mu$ and $\hat{H}_{el}$ on the nuclear coordinates are not shown explicitly for notational convenience.

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11.1 Hartree-Fock Approximation and Roothaan Equation

A simple but limited derivation of the HF energy, for the case of atomic orbitals, was provided in Chap. 8. This chapter provides a more detailed derivation for more general cases [14, 42].

11.1.1 General Single Determinant State

Let us assume that the electronic state for the N_e electrons can be expressed as a single Slater determinant as follows:

$$|\Psi_{N_e}\rangle = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} |\psi_1(1)\rangle & |\psi_2(1)\rangle & \cdots & |\psi_{N_e}(1)\rangle \\ |\psi_1(2)\rangle & |\psi_2(2)\rangle & \cdots & |\psi_{N_e}(2)\rangle \\ \vdots & \vdots & \vdots & \vdots \\ |\psi_1(N_e)\rangle & |\psi_2(N_e)\rangle & \cdots & |\psi_{N_e}(N_e)\rangle \end{vmatrix}$$

$$= \frac{1}{\sqrt{N_e!}} \sum_{\hat{P}} (-1)^{N_P} \hat{P} \left(|\psi_1(1)\rangle |\psi_2(2)\rangle \cdots |\psi_{N_e}(N_e)\rangle \right), \qquad (11.4)$$

where $|\psi_k(\mu)\rangle$ is the kth single electron spin-orbit state for electron $\mu = 1, \cdots, N_e$, and $\hat{P}$ represents all distinct permutations of the N_e electrons, with N_P being the number of pairwise permutations equivalent to each permutation. It is assumed that all $|\psi_k(\mu)\rangle$'s are orthogonal. If not, it should be possible to find a transformation that makes them orthogonal since the starting spin-orbit states should be linearly independent [42]. Such a transformation only results in the difference in the prefactor of the Slater determinant. On the other hand, since the starting basis states for molecular electronic states are nonorthogonal in general, it is important to specify the condition for orthogonality in more detail as will become clear later.

First, let us calculate the expectation value of $\hat{H}_{el}$ with respect to $|\Psi_{N_e}\rangle$ as follows:

$$\langle \Psi_{N_e} | \hat{H}_{el} | \Psi_{N_e} \rangle = \frac{1}{N_e!} \sum_{\hat{P}} \sum_{\hat{P}'} (-1)^{N_P + N_{P'}} \hat{P} \left(\langle \psi_1(1) | \langle \psi_2(2) | \cdots \langle \psi_{N_e}(N_e) | \right)$$

$$\times \left\{ \sum_{\mu=1}^{N_e} \hat{h}_\mu + \frac{1}{2} \sum_{\mu=1}^{N_e} \sum_{\nu \neq \mu} \frac{1}{\hat{r}_{\mu\nu}} \right\} \hat{P}' \left(|\psi_1(1)\rangle |\psi_2(2)\rangle \cdots |\psi_{N_e}(N_e)\rangle \right). \quad (11.5)$$

First, the term involving sum over single electron terms can be simplified to

$$\frac{1}{N_e!}\sum_{\hat{P}}\sum_{\hat{P}'}(-1)^{N_P+N_{P'}}\hat{P}\left(\langle\psi_1(1)|\langle\psi_2(2)|\cdots\langle\psi_{N_e}(N_e)|\right)\left(\sum_{\mu=1}^{N_e}\hat{h}_\mu\right)$$
$$\times\hat{P}'\left(|\psi_1(1)\rangle|\psi_2(2)\rangle\cdots|\psi_{N_e}(N_e)\rangle\right)$$
$$=\sum_{\mu=1}^{N_e}\frac{1}{N_e!}(N_e-1)!\sum_{j=1}^{N_e}\langle\psi_j(\mu)|\hat{h}_\mu|\psi_j(\mu)\rangle$$
$$=\sum_{j=1}^{N_e}\langle\psi_j(1)|\hat{h}_1|\psi_j(1)\rangle. \tag{11.6}$$

Major steps leading to the final expression above are summarized below.

- The first equality results from the fact that there are N_e different ways to assign single electron state for the electron with index μ by the permutation $\hat{P}$.
- The single electron interaction term survives only when each realization of the permutation $\hat{P}'$ is exactly the same as that of $\hat{P}$. Otherwise, there are at least one spin-orbital states that are orthogonal for those electrons with indices different from μ.
- The $(N_e-1)!$ factor results from counting all possible ways of permuting the (N_e-1) electrons except for the μ electron.
- The second equality above results from the fact that the single electron term is independent of μ and can be replaced with 1.
- After this replacement, the summation over μ results in a factor of N_e, which is divided by the same factor in the remaining denominator.

Therefore,

$$\langle\Psi_{N_e}|\sum_{\mu=1}^{N_e}\hat{h}_\mu|\Psi_{N_e}\rangle=\sum_{j=1}^{N_e}\langle\psi_j(1)|\hat{h}_1|\psi_j(1)\rangle=\sum_{j=1}^{N_e}\langle\psi_j|\hat{h}|\psi_j\rangle, \tag{11.7}$$

where we have dropped electron index 1 for simplicity in the last expression.

On the other hand, the two electron terms in Eq. (11.5) simplifies to

$$\frac{1}{N_e!}\sum_{\hat{P}}\sum_{\hat{P}'}(-1)^{N_P+N_{P'}}\hat{P}\left(\langle\psi_1(1)|\langle\psi_2(2)|\cdots\langle\psi_{N_e}(N_e)|\right)$$
$$\times\left\{\frac{1}{2}\sum_{\mu=1}^{N_e}\sum_{\nu\neq\mu}\frac{1}{\hat{r}_{\mu\nu}}\right\}\hat{P}'\left(|\psi_1(1)\rangle|\psi_2(2)\rangle\cdots|\psi_{N_e}(N_e)\rangle\right)$$

$$= \frac{1}{2} \sum_{\mu=1}^{N_e} \sum_{\nu \neq \mu} \frac{1}{N_e(N_e-1)} \sum_{j=1}^{N_e} \sum_{k \neq j} \left(\langle \psi_j(\mu) | \langle \psi_k(\nu) | \frac{1}{\hat{r}_{\mu\nu}} | \psi_j(\mu) \rangle | \psi_k(\nu) \rangle \right.$$
$$\left. - \langle \psi_j(\mu) | \langle \psi_k(\nu) | \frac{1}{\hat{r}_{\mu\nu}} | \psi_k(\mu) \rangle | \psi_j(\nu) \rangle \right)$$
$$= \frac{1}{2} \sum_{j=1}^{N_e} \sum_{k=1}^{N_e} \left(\langle \psi_j(1) | \langle \psi_k(2) | \frac{1}{\hat{r}_{12}} | \psi_j(1) \rangle | \psi_k(2) \rangle \right.$$
$$\left. - \langle \psi_j(1) | \langle \psi_k(2) | \frac{1}{\hat{r}_{12}} | \psi_k(1) \rangle | \psi_j(2) \rangle \right) . \tag{11.8}$$

The final expression above is obtained through a procedure described below.

- In the first equality of the above identities, the summation over j and k represent all distinct single electron spin-orbital states assigned to μ and ν electrons out of the permutation $\hat{P}$. There are $(N_e - 2)!$ ways of permuting electrons other than these two. These, when divided with the denominator, result in $(N_e - 2)!/N_e! = 1/N_e(N_e - 1)$.
- Out of all realizations of the permutation $\hat{P}'$, only those that are exactly the same as those from $\hat{P}$ and those for which the spin-orbital states for μ and ν electrons are interchanged survive because, for other permutations, there are at least one electron (other than μ and ν) that involves overlap of two orthogonal spin-orbit states.
- The permutation of $\hat{P}'$, which differs from $\hat{P}$ only by the exchange of two spin-orbit states involves one additional exchange compared to $\hat{P}$. Therefore, $(-1)^{N_P+N_{P'}} = -1$ for this case, which explains the negative sign of the second term.
- The second equality results from the fact that the indices μ and ν, being dummy indices, can be replaced with 1 and 2 without affecting the final outcome. The summation over μ and ν thus results in $N_e(N_e - 1)$ factor, which is divided by exactly the same factor in the remaining denominator.
- In the second equality, the case with $j = k$ was added since the two-electron terms in this case cancel out and do not contribute to the summation.

For more compact expression of the two-electron interaction terms, let us use simpler notations that are consistent with conventional definitions used in electronic structure theory as described below.

Notations for Two Electron Terms

Since the two electron interaction terms commonly involve the same Coulomb operator and electron indices 1 and 2 are dummy variables, we can express all the two-electron interaction terms as follows:

(continued)

$$
\begin{aligned}
\langle\psi_j\psi_k|\psi_{j'}\psi_{k'}\rangle &= \langle\psi_j(1)|\langle\psi_k(2)|\frac{1}{\hat{r}_{12}}|\psi_{j'}(1)\rangle|\psi_{k'}(2)\rangle \\
&= (\psi_j\psi_{j'}|\psi_k\psi_{k'}). \qquad (11.9)
\end{aligned}
$$

Note that $\langle\psi_j\psi_k|\psi_{j'}\psi_{k'}\rangle = \langle\psi_k\psi_j|\psi_{k'}\psi_{j'}\rangle$ since the exchange of 1 and 2 for both ket and bra does not cause any difference. The second equality above introduces so called chemist's notation, and is intuitively useful because bra and kets for the same electron are placed together. Note that $(\psi_j\psi_{j'}|\psi_k\psi_{k'}) = (\psi_k\psi_{k'}|\psi_j\psi_{j'})$ for this case.

Let us also define the following difference term:

$$
\begin{aligned}
\langle\psi_j\psi_k||\psi_{j'}\psi_{k'}\rangle &= \langle\psi_j\psi_k|\psi_{j'}\psi_{k'}\rangle - \langle\psi_j\psi_k|\psi_{k'}\psi_{j'}\rangle \\
&= \langle\psi_j\psi_k|\psi_{j'}\psi_{k'}\rangle - \langle\psi_k\psi_j|\psi_{j'}\psi_{k'}\rangle \\
&= \langle\psi_k\psi_j|\psi_{k'}\psi_{j'}\rangle - \langle\psi_k\psi_j|\psi_{j'}\psi_{k'}\rangle \\
&= \langle\psi_k\psi_j|\psi_{k'}\psi_{j'}\rangle - \langle\psi_j\psi_k|\psi_{k'}\psi_{j'}\rangle. \qquad (11.10)
\end{aligned}
$$

Combining Eqs. (11.7) and (11.8) and employing the two-electron integrals introduced above, we find that Eq. (11.5) can be expressed as

$$
\begin{aligned}
E_{el}^{HF} &= \sum_{j=1}^{N_e}\langle\psi_j|\hat{h}|\psi_j\rangle + \frac{1}{2}\sum_{j=1}^{N_e}\sum_{k=1}^{N_e}\left(\langle\psi_j\psi_k|\psi_j\psi_k\rangle - \langle\psi_j\psi_k|\psi_k\psi_j\rangle\right) \\
&= \sum_{j=1}^{N_e}\langle\psi_j|\hat{h}|\psi_j\rangle + \frac{1}{2}\sum_{j=1}^{N_e}\sum_{k=1}^{N_e}\langle\psi_j\psi_k||\psi_j\psi_k\rangle. \qquad (11.11)
\end{aligned}
$$

The above expression has been derived under the assumption that all the single electron states are orthogonal. Therefore, the following conditions have to be ensured.

$$
\langle\psi_j|\psi_k\rangle = \delta_{jk}. \qquad (11.12)
$$

Thus, employing the Lagrange multiplier method [19, 43] to incorporate the above constraint, we can find out the best approximation for the energy with this constraint employing a Lagrangian $\mathcal{L}$ defined as follows:

$$
\mathcal{L} = \sum_{j=1}^{N_e}\langle\psi_j|\hat{h}|\psi_j\rangle + \frac{1}{2}\sum_{j=1}^{N_e}\sum_{k=1}^{N_e}\langle\psi_j\psi_k||\psi_j\psi_k\rangle - \sum_{j=1}^{N_e}\sum_{k=1}^{N_e}\lambda_{jk}(\langle\psi_j|\psi_k\rangle - \delta_{jk}). \qquad (11.13)
$$

where λ_{jk}'s are as yet unknown Lagrange multipliers to be determined. Now, consider the variation of $\mathcal{L}$ as a functional of all $|\psi_j\rangle$'s and $\langle\psi_j|$'s as follows:

$$\begin{aligned}\delta\mathcal{L} &= \sum_j \left\{ \langle\delta\psi_j|\hat{h}|\psi_j\rangle + \langle\psi_j|\hat{h}|\delta\psi_j\rangle \right\} \\ &\quad + \frac{1}{2}\sum_{j=1}^{N_e}\sum_{k=1}^{N_e} \{ \langle\delta\psi_j\psi_k||\psi_j\psi_k\rangle + \langle\psi_j\delta\psi_k||\psi_j\psi_k\rangle \\ &\qquad + \langle\psi_j\psi_k||\delta\psi_j\psi_k\rangle + \langle\psi_j\psi_k||\psi_j\delta\psi_k\rangle \} \\ &\quad - \sum_{j=1}^{N_e}\sum_{k=1}^{N_e} \lambda_{jk}\left(\langle\delta\psi_j|\psi_k\rangle + \langle\psi_j|\delta\psi_k\rangle\right) = 0. \end{aligned} \tag{11.14}$$

In the second double summation of the above expression, $\langle\psi_j\delta\psi_k||\psi_j\psi_k\rangle = \langle\delta\psi_k\psi_j||\psi_k\psi_j\rangle$ and $\langle\psi_j\psi_k||\psi_j\delta\psi_k\rangle = \langle\psi_k\psi_j||\delta\psi_k\psi_j\rangle$. The exchange of the dummy summation indices j and k in these terms thus make these identical to other two electron terms. Thus, the above expression is equivalent to

$$\begin{aligned}\delta\mathcal{L} = \sum_j &\left\{ \langle\delta\psi_j|\hat{h}|\psi_j\rangle + \sum_{k=1}^{N_e}\left(\langle\delta\psi_j\psi_k||\psi_j\psi_k\rangle - \lambda_{jk}\langle\delta\psi_j|\psi_k\rangle\right) \right. \\ &\left. + \langle\psi_j|\hat{h}|\delta\psi_j\rangle + \sum_{k=1}^{N_e}\left(\langle\psi_j\psi_k||\delta\psi_j\psi_k\rangle - \lambda_{kj}\langle\psi_k|\delta\psi_j\rangle\right) \right\} = 0, \end{aligned} \tag{11.15}$$

where the indices j and k in the last term of Eq. (11.14) were interchanged, resulting in $\lambda_{kj}\langle\psi_k|\delta\psi_j\rangle$.

Let us consider two electron terms in Eq. (11.15) in more detail, which is given by

$$\begin{aligned}\langle\delta\psi_j\psi_k||\psi_j\psi_k\rangle &= \langle\delta\psi_j(1)|\langle\psi_k(2)|\frac{1}{\hat{r}_{12}}|\psi_j(1)\rangle|\psi_k(2)\rangle \\ &\quad - \langle\delta\psi_j(1)|\langle\psi_k(2)|\frac{1}{\hat{r}_{12}}|\psi_k(1)\rangle|\psi_j(2)\rangle. \end{aligned} \tag{11.16}$$

These can also be expressed in terms of effective single electron operators as follows:

$$\hat{\mathcal{J}}_1[\psi_k]|\psi_j(1)\rangle = \left(\langle\psi_k(2)|\frac{1}{\hat{r}_{12}}|\psi_k(2)\rangle\right)|\psi_j(1)\rangle, \tag{11.17}$$

$$\hat{\mathcal{K}}_1[\psi_k]|\psi_j(1)\rangle = \left(\langle\psi_k(2)|\frac{1}{\hat{r}_{12}}|\psi_j(2)\rangle \right)|\psi_k(1)\rangle, \tag{11.18}$$

where $\hat{\mathcal{J}}_1[\psi_k]|\psi_j(1)\rangle$ and $\hat{\mathcal{K}}_1[\psi_k]|\psi_j(1)\rangle$ are Coulomb and exchange interaction operators. These are functionals of as yet undetermined state $|\psi_k(2)\rangle$ for electron 2 while being operators on the state $|\psi_j(1)\rangle$ of the electron 1. Employing these, Eq. (11.16) can be expressed as

$$\langle\delta\psi_j\psi_k||\psi_j\psi_k\rangle = \langle\delta\psi_j(1)|(\hat{\mathcal{J}}_1[\psi_k] - \hat{\mathcal{K}}_1[\psi_k])|\psi_j(1)\rangle. \tag{11.19}$$

Similarly,

$$\langle\psi_j\psi_k||\delta\psi_j\psi_k\rangle = \langle\psi_j(1)|(\hat{\mathcal{J}}_1[\psi_k] - \hat{\mathcal{K}}_1[\psi_k])|\delta\psi_j(1)\rangle. \tag{11.20}$$

Therefore, Eq. (11.15) can be expressed as

$$\begin{aligned}\delta\mathcal{L} = &\sum_j \langle\delta\psi_j(1)| \left\{ \left(\hat{h}_1 + \sum_{k=1}^{N_e} (\hat{\mathcal{J}}_1[\psi_k] - \hat{\mathcal{K}}_1[\psi_k]) \right) |\psi_j(1)\rangle - \sum_{k=1}^{N_e} \lambda_{jk}|\psi_k(1)\rangle \right\} \\ &+ \sum_j \left\{ \langle\psi_j(1)| \left(\hat{h}_1 + \sum_{k=1}^{N_e} (\hat{\mathcal{J}}_1[\psi_k] - \hat{\mathcal{K}}_1[\psi_k]) \right) - \sum_{k=1}^{N_e} \langle\psi_k(1)|\lambda_{kj} \right\} |\delta\psi_j(1)\rangle \\ = &\ 0.\end{aligned} \tag{11.21}$$

If the states $|\psi_j\rangle$ are those minimizing the energy under the constraint, Eq. (11.21) has to be satisfied regardless of any variations of them, $|\delta\psi_j\rangle$ and $\langle\delta\psi_j|$, which can be viewed as being independent of each other. This means that the following two effective single electron equations have to be satisfied.

$$\left(\hat{h}_1 + \sum_{k=1}^{N_e} (\hat{\mathcal{J}}_1[\psi_k] - \hat{\mathcal{K}}_1[\psi_k]) \right) |\psi_j(1)\rangle = \sum_{k=1}^{N_e} \lambda_{jk}|\psi_k(1)\rangle, \tag{11.22}$$

$$\langle\psi_j(1)| \left(\hat{h}_1 + \sum_{k=1}^{N_e} (\hat{\mathcal{J}}_1[\psi_k] - \hat{\mathcal{K}}_1[\psi_k]) \right) = \sum_{k=1}^{N_e} \langle\psi_k(1)|\lambda_{kj}. \tag{11.23}$$

Note that $\hat{h}_1$, $\hat{\mathcal{J}}_1[\psi_k]$, and $\hat{\mathcal{K}}_1[\psi_k]$ are Hermitian operators. Therefore, taking Hermitian adjoint of Eq. (11.22), we find that

$$\langle\psi_j(1)| \left(\hat{h}_1 + \sum_{k=1}^{N_e} (\hat{\mathcal{J}}_1[\psi_k] - \hat{\mathcal{K}}_1[\psi_k]) \right) = \sum_{k=1}^{N_e} \langle\psi_k(1)|\lambda_{jk}^*. \tag{11.24}$$

Comparing this with Eq. (11.23), we find that $\lambda_{jk}^* = \lambda_{kj}$. Thus, λ_{jk}'s are components of a Hermitian matrix, which has real eigenvalues. Thus, solving Eq. (11.22) is sufficient for finding the solution of the HF approximation.

Equation (11.22) is similar to an eigenvalue problem, but is not yet in a conventional form because λ_{jk}'s form a non-diagonal matrix. However, since this matrix is Hermitian, it is possible to find a unitary transformation such that it becomes diagonal. For this, let us introduce the following Fock operator :

$$\hat{\mathcal{F}}_1[\psi] = \hat{h}_1 + \sum_{k=1}^{N_e} \left(\hat{\mathcal{J}}_1[\psi_k] - \hat{\mathcal{K}}_1[\psi_k] \right). \tag{11.25}$$

Thus, Eq. (11.22) can be expressed as

$$\hat{\mathcal{F}}_1[\psi]|\psi_j(1)\rangle = \sum_{k=1}^{N_e} \lambda_{jk}|\psi_k(1)\rangle, \text{ for } j = 1, \cdots, N_e \tag{11.26}$$

Since the matrix consisting of the λ_{jk} as its elements, which we denote here as $\mathbf{\Lambda}$, is Hermitian, there always exist normalized eigenvectors $\mathbf{u}_1, \cdots, \mathbf{u}_{N_e}$ with eigenvalues $\mathcal{E}_1, \cdots, \mathcal{E}_{N_e}$ such that

$$\mathbf{\Lambda}\mathbf{u}_k = \mathcal{E}_k\mathbf{u}_k, \text{ for } k = 1, \cdots, N_e \tag{11.27}$$

Let us define a transformation matrix $\mathbf{U} = (\mathbf{u}_1, \cdots, \mathbf{u}_{N_e})$, for which $U_{jk} = (\mathbf{u}_k)_j$. Then, $\mathbf{U}^\dagger\mathbf{U} = I$, where I is the identity matrix with dimension N_e, and transforms $\mathbf{\Lambda}$ to diagonal form as follows:

$$\mathbf{U}^\dagger\mathbf{\Lambda}\mathbf{U} = \mathbf{U}^\dagger\mathbf{U}\mathcal{E} = \mathcal{E}, \tag{11.28}$$

where $\mathcal{E}$ is the diagonal matrix with the $\mathcal{E}_k$ as its diagonal elements. It is also possible to prove that $\mathbf{U}\mathbf{U}^\dagger = I$. Thus, $\mathbf{U}$ is a unitary matrix.

Now, let us consider the following vector notation for Eq.(11.26).

$$\hat{\mathcal{F}}_1[\psi] \begin{pmatrix} |\psi_1(1)\rangle \\ |\psi_2(1)\rangle \\ \vdots \\ |\psi_{N_e}(1)\rangle \end{pmatrix} = \mathbf{\Lambda} \begin{pmatrix} |\psi_1(1)\rangle \\ |\psi_2(1)\rangle \\ \vdots \\ |\psi_{N_e}(1)\rangle \end{pmatrix}. \tag{11.29}$$

In the above expression, note that $\hat{F}_1[\psi]$ is a linear quantum mechanical operator that applies to each component state. Therefore, applying $\mathbf{U}^\dagger$ on both sides, we obtain

$$\hat{\mathcal{F}}_1[\psi]\mathbf{U}^\dagger \begin{pmatrix} |\psi_1(1)\rangle \\ |\psi_2(1)\rangle \\ \vdots \\ |\psi_{N_e}(1)\rangle \end{pmatrix} = \mathbf{U}^\dagger \mathbf{\Lambda} \mathbf{U} \mathbf{U}^\dagger \begin{pmatrix} |\psi_1(1)\rangle \\ |\psi_2(1)\rangle \\ \vdots \\ |\psi_{N_e}(1)\rangle \end{pmatrix} = \mathcal{E}\mathbf{U}^\dagger \begin{pmatrix} |\psi_1(1)\rangle \\ |\psi_2(1)\rangle \\ \vdots \\ |\psi_{N_e}(1)\rangle \end{pmatrix}. \tag{11.30}$$

Note that we have used the fact that $\hat{\mathcal{F}}_1[\psi]$ and $\mathbf{U}^\dagger$ commute with each other, since the former is a quantum mechanical operator whereas the latter is a matrix being applied to the vector of states. The identity of Eq. (11.28) has also been used.

Let us now define,

$$|\psi'_j(1)\rangle = \sum_{k=1}^{N_e} \left(\mathbf{U}^\dagger\right)_{jk} |\psi_k(1)\rangle. \tag{11.31}$$

Then, Eq. (11.30) implies that

$$\hat{\mathcal{F}}_1[\psi]|\psi'_j(1)\rangle = \mathcal{E}_j|\psi'_j(1)\rangle, \text{ for } j = 1, \cdots, N_e \tag{11.32}$$

In the above expression, note that $\hat{\mathcal{F}}_1$ is defined in terms of untransformed states. However, it turns out that it is equivalent to one expressed in terms of transformed states. This can be shown using the definition of $\hat{\mathcal{F}}_1$ directly. Since $\hat{h}_1$ is independent of states, we only need to consider the two electron terms. Thus, for an arbitrary state $|\psi''(1)\rangle$, the following identity can be established.

$$\begin{aligned}
&\sum_{k=1}^{N_e}(\hat{\mathcal{J}}_1[\psi_k] - \hat{\mathcal{K}}_1[\psi_k])|\psi''(1)\rangle \\
&= \sum_{k=1}^{N_e}\left\{\langle\psi_k(2)|\frac{1}{\hat{r}_{12}}|\psi_k(2)\rangle|\psi''(1)\rangle - \langle\psi_k(2)|\frac{1}{\hat{r}_{12}}|\psi''(2)\rangle|\psi_k(1)\rangle\right\} \\
&= \sum_{j=1}^{N_e}\sum_{j'=1}^{N_e}\sum_{k=1}^{N_e} U^*_{kj}U_{kj'}\left\{\langle\psi'_j(2)|\frac{1}{\hat{r}_{12}}|\psi'_{j'}(2)\rangle|\psi''(1)\rangle\right. \\
&\qquad \left. -\langle\psi'_j(2)|\frac{1}{\hat{r}_{12}}|\psi''(2)\rangle|\psi'_{j'}(1)\rangle\right\} \\
&= \sum_{j=1}^{N_e}\left\{\langle\psi'_j(2)|\frac{1}{\hat{r}_{12}}|\psi'_j(2)\rangle|\psi''(1)\rangle - \langle\psi'_j(2)|\frac{1}{\hat{r}_{12}}|\psi''(2)\rangle|\psi'_j(1)\rangle\right\} \\
&= \sum_{k=1}^{N_e}(\hat{\mathcal{J}}_1[\psi'_k] - \hat{\mathcal{K}}_1[\psi'_k])|\psi''(1)\rangle,
\end{aligned} \tag{11.33}$$

where the fact that $|\psi_k(1)\rangle = \sum_{kj} U_{kj}|\psi'_j(1)\rangle$ and the unitarity of $\mathbf{U}$ have been used. Therefore, $\hat{\mathcal{F}}_1[\psi]$ in Eq. (11.26) can be replaced with $\hat{\mathcal{F}}_1[\psi']$.

Note that the transformation from $|\psi_j(1)\rangle$ to $|\psi'_j(1)\rangle$ by the unitary transformation changes the Slater determinant state, Eq. (11.4), only by a complex factor of unit magnitude since the determinant of $\mathbf{U}$ is a complex number with unit magnitude. Therefore, the transformation does not affect the actual many electron states either [14, 42]. Therefore, without losing generality, we can replace $|\psi'_j(1)\rangle$ in Eq. (11.26) with $|\psi_j(1)\rangle$. The resulting equation is known as the canonical form of the HF equation and is summarized below.

Canonical Form of the HF Equation

The slater determinant state for many electrons, Eq. (11.4), which minimizes the total electronic energy, consists of the $|\psi_j\rangle$ that satisfy the following canonical HF equation:

$$\hat{\mathcal{F}}_1[\psi]|\psi_j(1)\rangle = (\hat{h}_1 + \sum_{k=1}^{N_e}(\hat{\mathcal{J}}_1[\psi_k] - \hat{\mathcal{K}}_1[\psi_k])|\psi_j(1)\rangle = \mathcal{E}_j|\psi_j(1)\rangle, \tag{11.34}$$

where $j = 1, \cdots, N_e$. Note that all the states are orthogonal and satisfy the condition of Eq. (11.12).

Taking inner product of Eq. (11.34) with $\langle\psi_j(1)|$, we obtain the following expression for the energy of the state $\mathcal{E}_j$:

$$\begin{aligned}
\mathcal{E}_j &= \langle\psi_j(1)|\hat{\mathcal{F}}_1[\psi]|\psi_j(1)\rangle \\
&= \langle\psi_j(1)|\hat{h}_1|\psi_j(1)\rangle + \sum_{k=1}^{N_e}\langle\psi_j(1)|\hat{\mathcal{J}}_1[\psi_k]|\psi_j(1)\rangle - \langle\psi_j(1)|\hat{\mathcal{K}}_1[\psi_k]|\psi_j(1)\rangle \\
&= \langle\psi_j(1)|\hat{h}_1|\psi_j(1)\rangle + \sum_{k=1}^{N_e}\langle\psi_j\psi_k|\psi_j\psi_k\rangle - \langle\psi_j\psi_k|\psi_k\psi_j\rangle \\
&= \langle\psi_j(1)|\hat{h}_1|\psi_j(1)\rangle + \sum_{k=1}^{N_e}\langle\psi_j\psi_k||\psi_j\psi_k\rangle.
\end{aligned} \tag{11.35}$$

Thus, we find that the HF energy given by Eq. (11.11) is related to the sum of the $\mathcal{E}_j$ as follows:

$$E_{HF} = \sum_{j=1}^{N_e}\mathcal{E}_j - \frac{1}{2}\sum_{j=1}^{N_e}\sum_{k=1}^{N_e}\langle\psi_j\psi_k||\psi_j\psi_k\rangle. \tag{11.36}$$

In general, Eqs. (11.34) and (11.36) can be solved together in the following self-consistent manner.

1. Assume a set of trial $|\psi_j\rangle$.
2. Calculate $\hat{\mathcal{F}}_1[\psi]$ for the trial $|\psi_j\rangle$.
3. Determine the new $|\psi_j\rangle$ and $\mathcal{E}_j$ satisfying Eq. (11.34).
4. Repeat steps 2 and 3 until the HF energy, Eq. (11.36), has converged sufficiently.

11.1.2 Restricted HF Equation for Doubly Filled Orbital States

Let us now consider the simplest case where there are $N_e = 2N_r$ electrons doubly occupying N_r orbitals. Thus, for $p = 1, \cdots, N_r$, the spin-orbit states are expressed as

$$|\psi_{2p-1}(1)\rangle = |\phi_p(1)\rangle|\alpha(1)\rangle, \tag{11.37}$$

$$|\psi_{2p}(1)\rangle = |\phi_p(1)\rangle|\beta(1)\rangle, \tag{11.38}$$

where $|\phi_p(1)\rangle$ represents the spatial-orbital state $|\alpha(1)\rangle$ for electron labeled 1. On the other hand, $|\alpha(1)\rangle$ and $|\beta(1)\rangle$ represent spin up and down states, respectively, also for electron 1. Then, the two electron interaction operators can be expressed in terms of orbital states. First, the Coulomb interaction terms can be expressed as follows:

$$\begin{aligned}\hat{\mathcal{J}}_1[\psi_{2q-1}]|\phi_p(1)\rangle|\alpha(1)\rangle &= \langle\phi_q(2)|\frac{1}{\hat{r}_{12}}|\phi_q(2)\rangle|\phi_p(1)\rangle|\alpha(1)\rangle \\ &= \left(\hat{J}_1[\phi_q]|\phi_p(1)\rangle\right)|\alpha(1)\rangle,\end{aligned} \tag{11.39}$$

$$\begin{aligned}\hat{\mathcal{J}}_1[\psi_{2q}]|\phi_p(1)\rangle|\alpha(1)\rangle &= \langle\phi_q(2)|\frac{1}{\hat{r}_{12}}|\phi_q(2)\rangle|\phi_p(1)\rangle|\alpha(1)\rangle \\ &= \left(\hat{J}_1[\phi_q]|\phi_p(1)\rangle\right)|\alpha(1)\rangle,\end{aligned} \tag{11.40}$$

$$\begin{aligned}\hat{\mathcal{J}}_1[\psi_{2q-1}]|\phi_p(1)\rangle|\beta(1)\rangle &= \langle\phi_q(2)|\frac{1}{\hat{r}_{12}}|\phi_q(2)\rangle|\phi_p(1)\rangle|\beta(1)\rangle \\ &= \left(\hat{J}_1[\phi_q]|\phi_p(1)\rangle\right)|\beta(1)\rangle,\end{aligned} \tag{11.41}$$

$$\begin{aligned}\hat{\mathcal{J}}_1[\psi_{2q}]|\phi_p(1)\rangle|\beta(1)\rangle &= \langle\phi_q(2)|\frac{1}{\hat{r}_{12}}|\phi_q(2)\rangle|\phi_p(1)\rangle|\beta(1)\rangle \\ &= \left(\hat{J}_1[\phi_q]|\phi_p(1)\right)\rangle|\beta(1)\rangle,\end{aligned} \tag{11.42}$$

where $\hat{J}_1$ represents Coulomb interaction operator applied to spatial orbital only. On the other hand, only two of the following exchange terms are nonzero in general.

$$\hat{\mathcal{K}}_1[\psi_{2q-1}]|\phi_p(1)\rangle|\alpha(1)\rangle = \langle\phi_q(2)|\frac{1}{\hat{r}_{12}}|\phi_p(2)\rangle|\phi_q(1)|\alpha(1)\rangle$$
$$= \left(\hat{K}_1[\phi_q]|\phi_p(1)\rangle\right)|\alpha(1)\rangle, \quad (11.43)$$

$$\hat{\mathcal{K}}_1[\psi_{2q}]|\phi_p(1)\rangle|\beta(1)\rangle = \langle\phi_q(2)|\frac{1}{\hat{r}_{12}}|\phi_p(2)\rangle|\phi_q(1)\rangle|\beta(1)\rangle$$
$$= \left(\hat{K}_1[\phi_q]|\phi_q(1)\rangle\right)|\beta(1)\rangle, \quad (11.44)$$

where $\hat{K}_1$ represents exchange interaction operator applied to spatial orbital only. It is easy to show that the following two cases of exchange interaction operation vanish due to the orthogonality of spin states.

$$\hat{\mathcal{K}}_1[\psi_{2q}]|\phi_p(1)\rangle|\alpha(1)\rangle = 0, \quad (11.45)$$

$$\hat{\mathcal{K}}_1[\psi_{2q-1}]|\phi_p(1)\rangle|\beta(1)\rangle = 0. \quad (11.46)$$

Employing Eqs. (11.39)–(11.46) provided above, one can express all the two electron interaction terms for spin-orbit states in terms of those for spatial orbital states as follows:

$$\sum_{k=1}^{N_e}(\hat{\mathcal{J}}_1[\psi_k] - \hat{\mathcal{K}}_1[\psi_k])|\phi_p(1)\rangle|\alpha(1)\rangle$$
$$= \sum_{q=1}^{N_r}\left(\hat{\mathcal{J}}_1[\psi_{2q-1}] - \hat{\mathcal{K}}_1[\psi_{2q-1}] + \hat{\mathcal{J}}_1[\psi_{2q}] - \hat{\mathcal{K}}_1[\psi_{2q}]\right)|\phi_p(1)\rangle|\alpha(1)\rangle$$
$$= |\alpha(1)\rangle\sum_{q=1}^{N_r}\left(2\hat{J}_1[\phi_q] - \hat{K}_1[\phi_q]\right)|\phi_p(1)\rangle, \quad (11.47)$$

$$\sum_{k=1}^{N_e}(\hat{\mathcal{J}}_1[\psi_k] - \hat{\mathcal{K}}_1[\psi_k])|\phi_p(1)\rangle|\beta(1)\rangle$$
$$= \sum_{q=1}^{N_r}\left(\hat{\mathcal{J}}_1[\psi_{2q-1}] - \hat{\mathcal{K}}_1[\psi_{2q-1}] + \hat{\mathcal{J}}_1[\psi_{2q}] - \hat{\mathcal{K}}_1[\psi_{2q}]\right)|\phi_p(1)\rangle|\beta(1)\rangle$$
$$= |\beta(1)\rangle\sum_{q=1}^{N_r}\left(2\hat{J}_1[\phi_q] - \hat{K}_1[\phi_q]\right)|\phi_p(1)\rangle. \quad (11.48)$$

Taking inner products of the above expressions with either $\langle\alpha(1)|$ or $\langle\beta(1)|$ results in the same expression for two electron operations involving spatial orbitals. Thus, combining this with the remaining one electron term, one can obtain the canonical HF equation for spatial orbitals as summarized below.

Canonical Form of the HF Equation for Doubly Occupied Spatial Orbital States

Employing Eq. (11.47) (or Eq. (11.48)) in Eq. (11.34) and taking inner-product with $\langle\alpha(1)|$ (or $\langle\beta(1)|$), we obtain

$$\hat{F}_1[\phi]|\phi_p(1)\rangle = (\hat{h}_1 + \sum_{q=1}^{N_r}(2\hat{J}_1[\phi_q] - \hat{K}_1[\phi_q])|\phi_p(1)\rangle = \mathcal{E}_p|\phi_p(1)\rangle, \tag{11.49}$$

where $p = 1, \cdots, N_r$. Note that all the orbital states are orthogonal to each other.

Taking inner product of Eq. (11.49) with $\langle\phi_p(1)|$, we obtain the following expression for the orbital energy:

$$\begin{aligned}\mathcal{E}_p &= \langle\phi_p(1)|\hat{F}_1[\phi]|\phi_p(1)\rangle \\ &= \langle\phi_p(1)|\hat{h}_1|\phi_p(1)\rangle + \sum_{q=1}^{N_r}(2\langle\phi_p(1)|\hat{J}_1[\phi_q]|\phi_p(1)\rangle - \langle\phi_p(1)|\hat{K}_1[\phi_q])|\phi_p(1)\rangle \\ &= \langle\phi_p(1)|\hat{h}_1|\phi_p(1)\rangle + \sum_{q=1}^{N_r}(2\langle\phi_p\phi_q|\phi_p\phi_q\rangle - \langle\phi_p\phi_q|\phi_q\phi_p\rangle).\end{aligned} \tag{11.50}$$

On the other hand, following a procedure similar to that used for deriving the above HF equation, the HF energy, Eq. (11.11), for the present case can be expressed as

$$E_{HF} = 2\sum_{p=1}^{N_r}\langle\phi_p(1)|\hat{h}_1|\phi_p(1)\rangle + \sum_{p=1}^{N_r}\sum_{q=1}^{N_r}(2\langle\phi_p\phi_q|\phi_p\phi_q\rangle - \langle\phi_p\phi_q|\phi_q\phi_p\rangle). \tag{11.51}$$

Therefore,

$$E_{HF} = 2\sum_{p=1}^{N_r}\mathcal{E}_p - \sum_{p=1}^{N_r}\sum_{q=1}^{N_r}(2\langle\phi_p\phi_q|\phi_p\phi_q\rangle - \langle\phi_p\phi_q|\phi_q\phi_p\rangle). \tag{11.52}$$

In general, Eqs. (11.49) and (11.52) can be solved together in the following self-consistent manner.

1. Assume a set of trial $|\phi_p\rangle$.
2. Calculate $\hat{F}[\phi]$ for the trial $|\phi_p\rangle$.

3. Determine new the $|\phi_p\rangle$ and $\mathcal{E}_p$ satisfying the restricted HF equation, Eq. (11.49).
4. Repeat steps 2 and 3 until the HF energy, Eq. (11.52), has converged sufficiently.

11.1.3 Linear Combination of Basis States

The self-consistent procedure described in previous subsections for determining spin orbital or orbital states is simple in principle, but actual implementation in its most general form is a numerically challenging task. In order to address this issue, Roothaan [42] employed an approximation for the states as linear combinations of pre-defined basis states. The resulting equation, often called HF-Roothaan equation, amounts to solving matrix equation, and is more amenable for computation. Here, this approach is described for the case of doubly filled orbital states.

Let us assume that each orbital state can be approximated as a linear combination of N_s basis states $|\varphi_j(1)\rangle$, which are not necessarily orthogonal but are independent of each other. Then, we can in general create N_s orbital states out of them as follows:

$$|\phi_p(1)\rangle = \sum_{k=1}^{N_s} C_{kp}|\varphi_k(1)\rangle,\ \ p = 1, \cdots, N_s. \tag{11.53}$$

However, note that only N_r lowest energy orbital states will be used for calculating the Fock operator. Employing the above expression in Eq. (11.49), we obtain

$$\hat{F}_1[\phi]|\phi_p(1)\rangle = \sum_{k=1}^{N_s} C_{kp}\hat{F}_1[\phi]|\varphi_k(1)\rangle = \mathcal{E}_p \sum_{k=1}^{N_s} C_{kp}|\varphi_k(1)\rangle, \tag{11.54}$$

where $\mathcal{E}_p$ is now one of N_s possible orbital energies. This is due to the use of a finite basis and is in contrast to the fact that the number of orbital energies for the original HF equation can be infinite.

Taking inner product of Eq. (11.54) with $\langle\varphi_j(1)|$, we obtain

$$\begin{aligned}\langle\varphi_j(1)|\hat{F}_1[\phi]|\phi_p(1)\rangle &= \sum_{k=1}^{N_s} C_{kp}\langle\varphi_j(1)|\hat{F}_1[\phi]|\varphi_k(1)\rangle \\ &= \mathcal{E}_p \sum_{k=1}^{N_s} C_{kp}\langle\varphi_j(1)|\varphi_k(1)\rangle.\end{aligned} \tag{11.55}$$

Let us define

$$F_{jk} = \langle\varphi_j(1)|\hat{F}_1[\phi]|\varphi_k(1)\rangle, \tag{11.56}$$

$$S_{jk} = \langle\varphi_j(1)|\varphi_k(1)\rangle. \tag{11.57}$$

Then, Eq. (11.55) can be expressed as follows:

$$\sum_{k=1}^{N_s} \left(F_{jk} C_{kp} - S_{jk} C_{kp} \mathcal{E}_p \right) = 0, \tag{11.58}$$

where $j, p = 1, \cdots, N_s$. The above equation is called HF-Roothaan equation and has to be solved self consistently because the F_{jk}'s depend on the C_{kp}'s. The above equation can be written compactly in terms of a matrix equation as follows:

$$\mathbf{FC} - \mathbf{SC}\mathcal{E} = 0, \tag{11.59}$$

where $\mathcal{E}$ is a $N_s \times N_s$ diagonal matrix with its elements $\mathcal{E}_p$'s.

The matrix elements of the Fock operator, defined by Eq. (11.56), can be calculated as follows:

$$\begin{aligned} \langle \varphi_j(1) | \hat{F}_1[\phi] | \varphi_k(1) \rangle &= \langle \varphi_j(1) | \hat{h}(1) | \varphi_k(1) \rangle \\ &+ \sum_{q=1}^{N_r} \Big(2 \langle \varphi_j(1) | \hat{J}_1[\phi_q] | \varphi_k(1) \rangle - \langle \varphi_j(1) | \hat{K}_1[\phi_q] | \varphi_j(1) \rangle \Big), \end{aligned} \tag{11.60}$$

where

$$\begin{aligned} \langle \varphi_j(1) | \hat{J}_1[\phi_q] | \varphi_k(1) \rangle &= \langle \varphi_j \phi_q | \varphi_k \phi_q \rangle \\ &= \sum_{j'=1}^{N_s} \sum_{k'=1}^{N_s} C^*_{j'q} C_{k'q} \langle \varphi_j \varphi_{j'} | \varphi_k \varphi_{k'} \rangle, \end{aligned} \tag{11.61}$$

$$\begin{aligned} \langle \varphi_j(1) | \hat{K}_1[\phi_q] | \varphi_k(1) \rangle &= \langle \varphi_j \phi_q | \phi_q \varphi_k \rangle \\ &= \sum_{j'=1}^{N_s} \sum_{k'=1}^{N_s} C^*_{j'q} C_{k'q} \langle \varphi_j \varphi_{j'} | \varphi_{k'} \varphi_k \rangle. \end{aligned} \tag{11.62}$$

Therefore,

$$\begin{aligned} \langle \varphi_j(1) | \hat{F}_1[\phi] | \varphi_k(1) \rangle &= \langle \varphi_j(1) | \hat{h}(1) | \varphi_k(1) \rangle \\ &+ \sum_{j'=1}^{N_s} \sum_{k'=1}^{N_s} \sum_{q=1}^{N_r} C^*_{j'q} C_{k'q} \left(2 \langle \varphi_j \varphi_{j'} | \varphi_k \varphi_{k'} \rangle - \langle \varphi_j \varphi_{j'} | \varphi_{k'} \varphi_k \rangle \right). \end{aligned} \tag{11.63}$$

Let us introduce

$$P_{j'k'} = 2 \sum_{q=1}^{N_r} C^*_{j'q} C_{k'q}, \tag{11.64}$$

which are related to the density[1] of occupied electron states in the basis of $|\varphi_k\rangle$, and employ the chemist's notation for two electron integrals. Namely, let us use the fact that $\langle\varphi_j\varphi_{j'}|\varphi_k\varphi_{k'}\rangle = (\varphi_j\varphi_k|\varphi_{j'}\varphi_{k'})$ and $\langle\varphi_j\varphi_{j'}|\varphi_{k'}\varphi_k\rangle = (\varphi_j\varphi_{k'}|\varphi_{j'}\varphi_k)$. Then, Eq. (11.63) can also be expressed as

$$\langle\varphi_j(1)|\hat{F}_1[\phi]|\varphi_k(1)\rangle = \langle\varphi_j(1)|\hat{h}(1)|\varphi_k(1)\rangle + \sum_{j'=1}^{N_s}\sum_{k'=1}^{N_s} P_{j'k'}\left[(\varphi_j\varphi_k|\varphi_{j'}\varphi_{k'}) - \frac{1}{2}(\varphi_j\varphi_{k'}|\varphi_{j'}\varphi_k)\right]. \quad (11.65)$$

Thus, Eq. (11.59), along with Eq. (11.65), and Eq. (11.52), expressed in terms of the same basis orbital states, can be solved together in the following self-consistent manner:

1. Assume a set of trial C_{kp}.
2. Calculate $\hat{F}_1$ for the trial C_{kp}.
3. Determine the new C_{kp} and $\mathcal{E}_p$ satisfying the restricted HF equation, Eq. (11.59).
4. Repeat steps 2 and 3 until the HF energy, Eq. (11.52), has converged sufficiently.

Note that, among the N_s orbitals obtained, only the N_r lowest orbitals need to be occupied for the calculation of the ground electronic state within the HF approximation. Other $N_s - N_r$ orbitals are called virtual orbitals. The secular equations are then solved and iteration continues until satisfactory convergence is achieved.

11.1.4 Choice of Basis Functions

The choice of the best possible basis set is a key issue in actual numerical implementation of the HF method. This is because the computational cost of the HF method calculation increases as the fourth power of the number of basis functions in general. Thus, unless judicious choice of basis functions is made, numerical implementation of the HF method can become unwieldy quite easily. Decades of theoretical and computational research have been made for identifying efficient and accurate enough basis functions and for numerical verification of their accuracies [2, 14, 15, 44–46]. A comprehensive presentation of this topic goes beyond the scope of this book. Thus, only a few key points concerning the choice of basis functions are summarized below.

- Although using a set of orthogonal basis functions is mathematically convenient and is possible to some extent, using atom-centered orbital functions that are non-orthogonal in general turned out to be much more convenient and reliable

[1] The matrix of P_{jk}'s is known as the charge density matrix and plays an essential role in determining various chemical properties such as bond order, partial charges, and dipole moments, etc.

choice. For this, the approach of using the LCAO-MO approximation serves as an important starting point except that the primitive basis functions used for the linear combination are not necessarily the actual atomic orbital functions but rather are viewed as closely related to them.

- For qualitatively correct description of short and long range Coulomb interactions, using Slater-type basis functions , $r^{n-1}Y_{lm}(\theta,\phi)e^{-\zeta r}$, which decay exponentially with r, is the best choice in reproducing qualitatively correct behavior for large r. However, numerical evaluation of Coulomb interactions using Slater-type orbitals is costly due to slow convergence.
- Using Gaussian type basis functions , $x^p y^q z^r e^{-\alpha r^2}$, is much more efficient for the evaluation of Coulomb interactions in particular because the actual integrations can be done by utilizing analytic expressions in most cases. However, using a single Gaussian type function as a basis is not a good choice because it does not reproduce appropriate limiting behavior. As a solution for this, the idea of contraction was developed.
- A contracted Gaussian basis function is a linear combination of Gaussian-type functions with different exponents so as to best mimic a Slater type orbital. It turned out that combination of a few primitive Gaussian functions serves as a reasonable representation for a Slater-type orbital as far as the calculation of important physical quantities including the energy is concerned. The coefficients for forming a contracted Gaussian function are predetermined so as to best approximate a Slater-type orbital and remain fixed during a HF calculation.
- A typical and most widely used HF method is to approximate the MO as a linear combination of primitive and contracted Gaussian functions and to determine the coefficients of the linear combination for the determination of minimum energy.
- Application of the HF method is not limited to only calculation of the electronic state and its energy but is in fact used for identifying the structure of the molecules in the ground electronic state. This is because it is possible to include the variation of the molecular structure in the HF calculation so that the lowest possible energy can be obtained varying the structure of a molecule. This is typically known as *geometry optimization*.
- Although not necessary for the geometry optimization calculation of the ground state, second derivatives of the potential energy surface, which form the Hessian matrix (see Eq. (4.89)), around the determined structure serve as important verification of the validity of the calculation result. This is because existence of negative eigenvalues for the Hessian matrix indicates that the determined structure does not even correspond to a local minimum energy, let alone the global energy minimum[2]. Eigenvalues of the Hessian matrix for the optimized structure also provide key information on vibrational states of the molecule.

[2] We describe here only the ground state, but geometry optimization is also used for determining transition states, for which the Hessian matrix has negative eigenvalues, and for excited states as well.

11.1.5 Methods Beyond HF Approximation

Configuration interaction (CI) [2, 14, 15, 47] goes beyond the HF approximation by adding new excited state Slater determinants (configurations) where some of the virtual orbitals in the HF determinant have replaced lower occupied orbitals. The simplest of this is called CI singles (CIS), where only single occupation of only one virtual orbitals is considered. CI singles and doubles (CISD) on the other hand include all the slater determinants where one or two virtual orbitals are occupied.

It is known that the CI method can account for electronic correlation effects that are missing in HF reasonably well when their contributions are relatively small. However, for strongly correlated systems, convergence becomes slower and the calculation becomes unmanageable. Another fundamental issue of the CI methods is that it is not size consistent unless full contributions of CI are included. There are alternative approaches that are generally called many-body perturbation theories, the description of which requires more advanced formulations [2, 14, 15, 48].

It is also possible to use more than one determinants as the starting point for HF-like calculations, which is in general called multi-configuration (MC) SCF method. Any method that uses MC-SCF solution as the starting reference state, instead of a single determinant HF state, is called multi-reference method [15].

The CI methods and multi-reference methods based on MC-SCF can also be used for the calculation of excited electronic states. In addition, it is also possible to conduct further SCF procedure for the excited states as well. A well-known method is called complete active space SCF (CAS-SCF) [15], which focuses on active regions of orbitals. CAS perturbation theory (CAS-PT) conducts additional perturbation correction for CAS-SCF and can improve the accuracy significantly as well.

Among various electronic structure calculation methods that build on the HF approximation, the best but the most demanding method is called coupled cluster (CC) method [15, 48], which accounts for important many-electron interactions up to the infinite order based on theorems of diagrammatic expansion. The CC method can be based on either single or multi-reference. The CC method is often referred to as the gold standard and its full implementation employing multi-references is typically used for benchmarking other lower level approximations.

11.2 Density Functional Theory

Let us define $|\mathbf{r};\mu\rangle$ as the state where the position of electron μ is at $\mathbf{r}$. Then,

$$\int d\mathbf{r}|\mathbf{r};\mu\rangle\langle\mathbf{r};\mu| = \hat{1}_\mu, \tag{11.66}$$

where $\hat{1}_\mu$ is the identity operator in the Hilbert space of the spatial orbital states for electron μ. Here, we assume a little more general case where there can be external potential applied to each electron μ, $V_{ext}(\mathbf{r})$, in addition to the electron nuclei potential. Thus, we introduce

$$V(\mathbf{r}) = -\sum_{c=1}^{N_u} \int d\mathbf{r} \frac{Z_c}{|\mathbf{r} - \mathbf{R}_c|} + V_{ext}(\mathbf{r}). \tag{11.67}$$

It is straightforward to find position representations of the terms constituting the electronic Hamiltonian, Eq. (11.1), with the electron-nuclei potential replaced with the above single electron potential. First, the single electron term can be expressed as

$$\begin{aligned} \hat{h}_\mu &= \int d\mathbf{r} \int d\mathbf{r}' |\mathbf{r}; \mu\rangle\langle\mathbf{r}; \mu| \frac{\hat{\mathbf{p}}_\mu^2}{2} |\mathbf{r}'; \mu\rangle\langle\mathbf{r}'; \mu| + \int d\mathbf{r}\ V(\hat{\mathbf{r}}_\mu)|\mathbf{r}; \mu\rangle\langle\mathbf{r}; \mu| \\ &= -\int d\mathbf{r} \int d\mathbf{r}' |\mathbf{r}; \mu\rangle \frac{1}{2} \nabla_{\mathbf{r}}^2 \delta(\mathbf{r} - \mathbf{r}')\langle\mathbf{r}'; \mu| + \int d\mathbf{r}\ V(\mathbf{r})|\mathbf{r}; \mu\rangle\langle\mathbf{r}; \mu|. \end{aligned} \tag{11.68}$$

Second, the two electron term can be expressed as

$$\begin{aligned} \frac{1}{\hat{r}_{\mu\nu}} &= \int d\mathbf{r} \int d\mathbf{r}' \frac{1}{\hat{r}_{\mu\nu}} |\mathbf{r}, \mathbf{r}'; \mu, \nu\rangle\langle\mathbf{r}, \mathbf{r}'; \mu, \nu| \\ &= \int d\mathbf{r} \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} |\mathbf{r}, \mathbf{r}'; \mu, \nu\rangle\langle\mathbf{r}, \mathbf{r}'; \mu, \nu|, \end{aligned} \tag{11.69}$$

where $|\mathbf{r}, \mathbf{r}'; \mu, \nu\rangle \equiv |\mathbf{r}; \mu\rangle \otimes |\mathbf{r}'; \nu\rangle$.

Then, for arbitrary many-electron state $|\Psi_e\rangle$,

$$\begin{aligned} E_{el}(\Psi_e) &\equiv \langle\Psi_e|\hat{H}_{el}|\Psi_e\rangle \\ &= -\sum_{\mu=1}^{N_e} \int d\mathbf{r} \int d\mathbf{r}' \langle\Psi_e|\mathbf{r}; \mu\rangle \frac{1}{2} \nabla_{\mathbf{r}}^2 \delta(\mathbf{r} - \mathbf{r}')\langle\mathbf{r}'; \mu|\Psi_e\rangle \\ &+ \sum_{\mu=1}^{N_e} \int d\mathbf{r}\ V(\mathbf{r})\langle\Psi_e|\mathbf{r}; \mu\rangle\langle\mathbf{r}; \mu|\Psi_e\rangle \\ &+ \frac{1}{2} \sum_{\mu=1}^{N_e} \sum_{\nu\neq\mu} \int d\mathbf{r} \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \langle\Psi_e|\mathbf{r}, \mathbf{r}'; \mu, \nu\rangle\langle\mathbf{r}, \mathbf{r}'; \mu, \nu|\Psi_e\rangle. \end{aligned} \tag{11.70}$$

Let us define

$$\rho_1(\mathbf{r}) = \sum_{\mu=1}^{N_e} \langle \Psi_e | \mathbf{r}; \mu \rangle \langle \mathbf{r}; \mu | \Psi_e \rangle, \tag{11.71}$$

$$\rho_2(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \sum_{\mu=1}^{N_e} \sum_{\nu \neq \mu} \langle \Psi_e | \mathbf{r}, \mathbf{r}'; \mu, \nu \rangle \langle \mathbf{r}, \mathbf{r}'; \mu, \nu | \Psi_e \rangle. \tag{11.72}$$

In above expressions, $\rho_1(\mathbf{r})$ is the density to find an electron (one-electron density) at position $\mathbf{r}$ and $\rho_2(\mathbf{r}, \mathbf{r}')$ is the density to find an electron at position $\mathbf{r}$ and the other electron at $\mathbf{r}'$, which is called two-electron density. As expected, these satisfy the following normalization conditions:

$$\int d\mathbf{r}\ \rho_1(\mathbf{r}) = N_e, \tag{11.73}$$

$$\int d\mathbf{r} \int d\mathbf{r}'\ \rho_2(\mathbf{r}, \mathbf{r}') = \frac{N_e(N_e - 1)}{2}. \tag{11.74}$$

The above one and two electron densities can be viewed as diagonal elements of corresponding one and two electron density operators with their matrix elements defined as

$$\gamma_1(\mathbf{r}; \mathbf{r}') = \sum_{\mu=1}^{N_e} \langle \Psi_e | \mathbf{r}; \mu \rangle \langle \mathbf{r}'; \mu | \Psi_e \rangle, \tag{11.75}$$

$$\gamma_2(\mathbf{r}, \mathbf{r}'; \mathbf{r}'', \mathbf{r}''') = \frac{1}{2} \sum_{\mu=1}^{N_e} \sum_{\nu \neq \mu} \langle \Psi_e | \mathbf{r}, \mathbf{r}'; \mu, \nu \rangle \langle \mathbf{r}'', \mathbf{r}'''; \mu, \nu | \Psi_e \rangle. \tag{11.76}$$

It is clear that $\rho_1(\mathbf{r}) = \gamma_1(\mathbf{r}; \mathbf{r})$ and $\rho_2(\mathbf{r}, \mathbf{r}') = \gamma_2(\mathbf{r}, \mathbf{r}'; \mathbf{r}, \mathbf{r}')$. It is not difficult to find that $\gamma_1(\mathbf{r}; \mathbf{r}')$ is a sum of matrix elements of the density operator, $|\Psi_e\rangle\langle\Psi_e|$, reduced to a single electron position space and that $\gamma_2(\mathbf{r}, \mathbf{r}'; \mathbf{r}'', \mathbf{r}''')$ is that reduced to two electron position space.

The average energy of the many-electron state, Eq. (11.70), can be expressed in terms of electron densities and density matrix elements, as follows:

$$E_{el}(\Psi_e) = -\int d\mathbf{r} \int d\mathbf{r}' \gamma_1(\mathbf{r}; \mathbf{r}') \frac{1}{2} \nabla_{\mathbf{r}}^2 \delta(\mathbf{r} - \mathbf{r}') + \int d\mathbf{r}\ V(\mathbf{r}) \rho_1(\mathbf{r}) + \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho_2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \tag{11.77}$$

which appears to be much simpler than the original expression. The above expression shows that the information on $\gamma_1(\mathbf{r}; \mathbf{r}')$, $\rho_1(\mathbf{r})$, $\rho_2(\mathbf{r}, \mathbf{r}')$ and $V(\mathbf{r})$ completely

determines the energy. Since all the three densities are completely determined from $|\Psi_e\rangle$'s, which are in turn fully determined once $V(\mathbf{r})$ is known because all other terms are intrinsic properties of the many electron system, all possible values of E_{el} and corresponding states can be considered as different functionals of $V(\mathbf{r})$.

For the ground electronic state $|\Psi_{e,g}\rangle$ or its energy $E_{el,g}$, which can be viewed as a unique functional of $V(\mathbf{r})$, stronger statement is in fact possible. It turns out that the ground electronic state or energy can be viewed as a unique functional of $\rho_1(\mathbf{r})$. An elegant proof for this was first demonstrated by Hohenberg and Kohn [49].

Theorem 11.1 *For any system with fixed number of electrons, the potential energy* $V(\mathbf{r})$ *is a unique functional of the one-particle electron density,* $\rho_{1,g}(\mathbf{r})$*, for the ground electronic state* $|\Psi_{e,g}\rangle$*.*

Proof If $V(\mathbf{r})$ is not a unique functional of $\rho_{1,g}(\mathbf{r})$, the former cannot be determined even if the latter is known. This means that there can be multiple $V(\mathbf{r})$'s for the same $\rho_{1,g}(\mathbf{r})$. Thus, let us take two potentials $V(\mathbf{r})$ and $V'(\mathbf{r})$, which differ by more than a constant but correspond to the same $\rho_{1,g}(\mathbf{r})$. Let us denote the electronic Hamiltonian for the two potentials as $\hat{H}_{el}$ and $\hat{H}'_{el}$. Note that the following relationship between these two Hamiltonians holds:

$$\hat{H}_{el} - \hat{H}'_{el} = V(\hat{\mathbf{r}}) - V'(\hat{\mathbf{r}}). \tag{11.78}$$

Let us also denote the ground electronic states for the two Hamiltonians respectively as $|\Psi_{e,g}\rangle$ and $|\Psi'_{e,g}\rangle$, which however corresponds to the same $\rho_{1,g}(\mathbf{r})$. Since the two potentials differ by more than a constant, $|\Psi_{e,g}\rangle$ and $|\Psi'_{e,g}\rangle$ should be different.

Let us first consider the fact that $E'_{el,g}$ is the eigenvalue of the ground electronic state $|\Psi'_{e,g}\rangle$ for $\hat{H}'_{el}$. As shown in Chap. 7, this means the following inequality:

$$\begin{aligned}E'_{el,g} &= \langle\Psi'_{e,g}|\hat{H}'|\Psi'_{e,g}\rangle \\ &< \langle\Psi_{e,g}|\hat{H}'|\Psi_{e,g}\rangle = \langle\Psi_{e,g}|(\hat{H} + \hat{V}' - \hat{V})|\Psi_{e,g}\rangle \\ &= E_{el,g} + \int d\mathbf{r}\, \rho_{1,g}(\mathbf{r})(V'(\mathbf{r}) - V(\mathbf{r})),\end{aligned} \tag{11.79}$$

where the fact that the effect of the potential can be fully accounted for by the single electron density has been used. Similarly, switching between the two states above, we also find that

$$\begin{aligned}E_{el,g} &= \langle\Psi_{e,g}|\hat{H}|\Psi_{e,g}\rangle \\ &< \langle\Psi'_{e,g}|\hat{H}|\Psi'_{e,g}\rangle = \langle\Psi'_{e,g}|(\hat{H}' - \hat{V}' + \hat{V})|\Psi'_{e,g}\rangle \\ &= E'_{el,g} - \int d\mathbf{r}\, \rho_{1,g}(\mathbf{r})(V'(\mathbf{r}) - V(\mathbf{r})).\end{aligned} \tag{11.80}$$

Adding the above two quantities, we find that

$$E'_{el,g} + E_{el,g} < E_{el,g} + E'_{el,g}, \tag{11.81}$$

which is contradictory. This means that $V(\mathbf{r})$ is uniquely determined up to an additive constant factor once $\rho_{1,g}(\mathbf{r})$ is known. Thus, $V(\mathbf{r})$ is a unique functional of $\rho_{1,g}(\mathbf{r})$. □

Since $|\Psi_{e,g}\rangle$ or $E_{el,g}$ is a unique functional of $V(\mathbf{r})$, the above theorem implies that it is also a unique functional of the ground state single electron density. This theorem leads to the density functional theory (DFT) [50] as summarized below.

Density Functional Theory (DFT)

- According to Hohenberg and Kohn [49], for a given system of fixed number of electrons, the ground state energy (up to an additive constant factor) is a unique functional of the single electron density. This implies that, if the exact form of the functional is known, only the information on the density is sufficient to determine the energy. However, this theorem is limited to the case where the energy can be represented as a unique functional of an external potential $V(\mathbf{r})$, which does not necessarily account for all possible electron densities.
- Mel Levy developed a general theorem [51], which overcame the limitation of the theorem by Hohenberg and Kohn and proved the existence of a universal functional for the ground state energy as a constrained minimum. This extended the applicability of DFT significantly.
- Kohn and Sham [52] used the variational theorem and derived the following effective one-electron equation:

$$\left\{ -\frac{1}{2}\nabla^2 + V(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{xc}(n(\mathbf{r}))}{\delta n(\mathbf{r}))} \right\} \psi_i(\mathbf{r}) = \mathcal{E}_i \psi_i(\mathbf{r}), \tag{11.82}$$

where atomic units were used and $n(\mathbf{r}) = \sum_i^{N_e} |\psi_i(\mathbf{r})|^2$, and $E_{xc}(n(\mathbf{r}))$ is the functional of exchange interaction. The above equation can be solved iteratively as long as the form of $E_{xc}(n(\mathbf{r}))$ is known. This approach is known as Kohn-Sham DFT and has served as the major approach in the application of DFT.

DFT as stated above is a powerful theory that allows calculation of almost infinite number of many electron systems by a simple set of equations if the exact functional form is known. This is a beautiful theoretical statement, but the exact form of the functional is impossible to know in practice. Over many decades, great advances have been made in devising approximate but fairly accurate forms of functional, which have established the DFT method as one of the most efficient and reliable electronic structure calculation methods [50, 53, 54].

Later, further extension of the above proof for the cases of time dependent potential was established, leading to time dependent DFT (TD-DFT) theory [55]. This theory states that any time dependent potential energy that can be expanded as polynomials of time variable can be shown to be a functional of the single electron density, which in turn allows calculation of the excited state properties in terms of the single electron density as well. Actual proof of TD-DFT is more involved and the implementation of the resulting TD-DFT method also requires additional set of new assumptions and approximations. As yet, this method has also made great progress and is now considered as one of the leading computational methods for the calculation of excited state properties.

11.3 Summary and Questions

For a many-electron state given by a Slater determinant of orthogonal single electron spin-orbit states such as Eq. (11.4), the expectation value of the electronic Hamiltonian, Eq. (11.11), is expressed as a sum of single electron and two electron terms. The latter two electron terms in turn consist of Coulomb interactions between electrons, which have classical analogues, and exchange interaction terms that have negative sign originating from the Pauli exclusion principle. Thus, these exchange interaction terms have purely quantum mechanical origin and are responsible for unique quantum mechanical properties of many-electron systems.

The simplification of the total electronic energy for many electron states, even though the Slater determinant involves all electronic states, reflects that the potential energy of the Hamiltonian has only one and two electron interactions. It is also an outcome of the orthogonality of single electron states, which changes only the coefficient of the Slater determinant and does not restrict the nature of many electron Slater determinant state. On the other hand, it is important that the condition of orthogonality has to be actually incorporated as constraints in applying the variational principle.

Application of the Lagrange multiplier method to combine the minimum energy requirement and the orthogonality condition, leads to a general form of the HF equation, Eq. (11.26). Further simplification of this equation into a canonical form, Eq. (11.34), can be made using the fact the a unitary transformation diagonalizing the Lagrange multiplier matrix $\mathbf{\Lambda}$ can be applied to single electron states, which does not alter the Slater determinant except for a numerical factor of unit magnitude. The canonical HF equation has the appearance of standard eigenvalue problem, but it in fact needs to be determined self consistently because both the Coulomb and exchange interaction operators are functionals of one-electron spin-orbit states yet to be determined.

Considering the types of spin states more explicitly, it is possible to reduce the canonical HF into a form that involves only spatial orbitals. For the case of singlet many-electron states where all the spatial orbitals are doubly occupied, the resulting expression is given by Eq. (11.49). In this expression, Coulomb terms have a factor

of 2 multiplied, which reflect two possible cases of single electron spins up and down that do not affect the spatial integral of the Coulomb potential energy. On the other hand, the exchange interaction terms do not have that factor. This is because the exchange interaction terms become zero when the two spin-orbit states being exchanged have opposite, thus orthogonal, spin states.

For developing efficient and general methods for solving the HF equation, it is convenient to introduce basis states that can represent single electron orbital states as their linear combinations. For a general nonorthogonal basis, the HF equation can thus be converted into a HF-Roothaan equation, Eq. (11.58), which are more amenable for numerical iterative procedures. In combination with the development of practical and efficient ways to construct a general class of basis functions, the HF method has been established as one of the most successful approaches for calculating the ground electronic state energy and determining the structure of polyatomic molecules. The HF method also serves as the starting point for more advanced calculations for general electronic states.

Alternatively, it is possible to express the electronic energy in terms of single and two electron densities as in Eq. (11.77). According to the proof by Hohenberg and Kohn, the ground electronic state energy can in fact be defined as a unique functional of a single electron density. This reduces calculating the ground state energy of many-electron system into determining the universal functional and the electron density that minimizes the energy for a given system, leading to the DFT method that serve as an important alternative to the direct wavefunction formulation. Extension of this perspective to the case of time dependent external potential led to the TD-DFT method, which now serves as one of the most widely approaches used for calculating the excited states of many polyatomic molecules.

Questions

- Is Fock operator always Hermitian regardless of the nature of basis set? If yes, does it also mean that it can be related to a physical observable?
- Under what conditions, a many-electron state cannot be represented by a single Slater determinant but requires linear combination of many Slater determinants at least?
- Under what conditions, a many-electron state cannot be represented even by a linear combinations of Slater determinants but requires description at the level of density operator?
- Can any electronic state energy of a general many-body system be uniquely determined once its single electron density is known?

Exercise Problems with Solutions

11.1 The Hamiltonian for a certain three-electron system is as follows:

$$\hat{H} = \hat{h}_1 + \hat{h}_2 + \hat{h}_3 + \frac{1}{\hat{r}_{12}} + \frac{1}{\hat{r}_{23}} + \frac{1}{\hat{r}_{31}},$$

where $\hat{h}_j$ with $j = 1, 2, 3$ are one electron Hamiltonians that are identical except for the index and $r_{jk} = |\mathbf{r}_j - \mathbf{r}_k|$ is the distance between electron j and electron k. The state of the three electrons is represented by the following Slater determinant:

$$|\Psi\rangle = \frac{1}{\sqrt{6}} \begin{vmatrix} |\psi_1(1)\rangle & |\psi_2(1)\rangle & |\psi_3(1)\rangle \\ |\psi_1(2)\rangle & |\psi_2(2)\rangle & |\psi_3(2)\rangle \\ |\psi_1(3)\rangle & |\psi_2(3)\rangle & |\psi_3(3)\rangle \end{vmatrix},$$

where $|\psi_k(j)\rangle$ is the kth single electron spin-orbit state with electron j. Answer the following questions.

(a) Calculate the determinant explicitly and express $|\Psi\rangle$ as a linear combination of direct products of the single electron spin-orbit states.
(b) Express $\langle\Psi| \left(\hat{h}_1+\hat{h}_2+\hat{h}_3\right) |\Psi\rangle$ in terms of the h_k where $h_k = \langle\psi_k(j)|\hat{h}_j|\psi_k(j)\rangle$
(c) Express $\langle\Psi| \left(\frac{1}{\hat{r}_{12}} + \frac{1}{\hat{r}_{23}} + \frac{1}{\hat{r}_{31}}\right) |\Psi\rangle$ in terms of all possible Coulomb and exchange interaction terms.

Solution 11.1

(a)

$$\begin{aligned} |\Psi\rangle = \frac{1}{\sqrt{6}} & (|\psi_1(1)\rangle|\psi_2(2)\rangle|\psi_3(3)\rangle + |\psi_2(1)\rangle|\psi_3(2)\rangle|\psi_1(3)\rangle \\ & + |\psi_3(1)\rangle|\psi_1(2)\rangle|\psi_2(3)\rangle \\ & - |\psi_3(1)\rangle|\psi_2(2)\rangle|\psi_1(3)\rangle - |\psi_1(1)\rangle|\psi_3(2)\rangle|\psi_2(3)\rangle \\ & - |\psi_2(1)\rangle|\psi_1(2)\rangle|\psi_3(3)\rangle) . \end{aligned}$$

(b)

$$\langle\Psi|\hat{h}_1|\Psi\rangle = \frac{1}{6}(h_1 + h_2 + h_3 + h_3 + h_1 + h_2) = \frac{1}{3}(h_1 + h_2 + h_3),$$

$$\langle\Psi|\hat{h}_2|\Psi\rangle = \frac{1}{6}(h_2 + h_3 + h_1 + h_2 + h_3 + h_1) = \frac{1}{3}(h_1 + h_2 + h_3),$$

$$\langle\Psi|\hat{h}_3|\Psi\rangle = \frac{1}{6}(h_3 + h_1 + h_2 + h_1 + h_2 + h_3) = \frac{1}{3}(h_1 + h_2 + h_3).$$

Therefore, $\langle\Psi|(\hat{h}_1 + \hat{h}_2 + \hat{h}_3)|\Psi\rangle = h_1 + h_2 + h_3$.

(c) Let us define

$$J_{jk} = \langle\psi_j(\mu)|\langle\psi_k(\nu)|\frac{1}{\hat{r}_{\mu\nu}}|\psi_j(\mu)\rangle|\psi_k(\nu)\rangle \;\&$$

$$K_{jk} = \langle\psi_j(\mu)|\langle\psi_k(\nu)|\frac{1}{\hat{r}_{\mu\nu}}|\psi_k(\mu)\rangle|\psi_j(\nu)\rangle,$$

which are the same for any μ and ν. Then,

$$\begin{aligned}
\langle\Psi|\frac{1}{\hat{r}_{12}}|\Psi\rangle &= \frac{1}{6}\left(J_{12} - K_{12} + J_{23} - K_{23} + J_{31} - K_{31}\right.\\
&\qquad \left.+J_{32} - K_{32} + J_{13} - K_{13} + J_{21} - K_{21}\right),\\
\langle\Psi|\frac{1}{\hat{r}_{23}}|\Psi\rangle &= \frac{1}{6}\left(J_{23} - K_{23} + J_{31} - K_{31} + J_{12} - K_{12} + J_{21} - K_{21}\right.\\
&\qquad \left.+J_{32} - K_{32} + J_{13} - K_{13}\right),\\
\langle\Psi|\frac{1}{\hat{r}_{31}}|\Psi\rangle &= \frac{1}{6}\left(J_{31} - K_{31} + J_{12} - K_{12} + J_{23} - K_{23} + J_{13} - K_{13}\right.\\
&\qquad \left.+J_{21} - K_{21} + J_{32} - K_{32}\right).
\end{aligned}$$

Since all three lines above the same and $J_{jk} = J_{kj}$ and $K_{jk} = K_{kj}$, we find that

$$\langle\Psi|\left(\frac{1}{\hat{r}_{12}} + \frac{1}{\hat{r}_{23}} + \frac{1}{\hat{r}_{23}}\right)|\Psi\rangle = J_{12} - K_{12} + J_{23} - K_{23} + J_{31} - K_{31}.$$

Problems

11.2 Prove that the Coulomb and exchange operators defined by Eqs. (11.17) and (11.18) are Hermitian.

11.3 Prove Eq. (11.51) explicitly.

11.4 The Hamiltonian for a certain four-electron system is as follows:

$$\hat{H} = \sum_{\mu=1}^{4}\hat{h}_\mu + \frac{1}{2}\sum_{\mu=1}^{4}\sum_{\nu\neq\mu}\frac{1}{\hat{r}_{\mu\nu}},$$

where the $\hat{h}_\mu$ are one electron Hamiltonians that are identical except for the index μ and $r_{\mu\nu} = |\mathbf{r}_\mu - \mathbf{r}_\nu|$ is the distance between electron μ and electron ν. The state of the four electrons is represented by the following slater determinant:

$$|\Psi\rangle = \frac{1}{\sqrt{24}} \begin{vmatrix} |\psi_1(1)\rangle & |\psi_2(1)\rangle & |\psi_3(1)\rangle & |\psi_4(1)\rangle \\ |\psi_1(2)\rangle & |\psi_2(2)\rangle & |\psi_3(2)\rangle & |\psi_4(2)\rangle \\ |\psi_1(3)\rangle & |\psi_2(3)\rangle & |\psi_3(3)\rangle & |\psi_4(3)\rangle \\ |\psi_1(4)\rangle & |\psi_2(4)\rangle & |\psi_3(4)\rangle & |\psi_4(4)\rangle \end{vmatrix},$$

where $|\psi_k(\mu)\rangle$ is the kth single electron spin-orbit state with electron μ. Answer the following questions.

(a) Calculate the determinant explicitly and express $|\Psi\rangle$ as a linear combination of direct products of the single electron spin-orbit states.
(b) Express $\langle\Psi| \left(\sum_{\mu=1}^{4} \hat{h}_\mu\right) |\Psi\rangle$ in terms of the h_k where $h_k = \langle\psi_k(\mu)|\hat{h}_\mu|\psi_k(\mu)\rangle$.
(c). Express $\langle\Psi|\hat{H}|\Psi\rangle$ in terms of the h_k and all possible Coulomb and exchange interaction terms.

11.5 Prove that the kinetic energy term in Eq. (11.77) satisfies the following identity:

$$\int d\mathbf{r} \int d\mathbf{r}' \gamma_1(\mathbf{r}; \mathbf{r}') \frac{1}{2} \nabla_{\mathbf{r}}^2 \delta(\mathbf{r} - \mathbf{r}') = \int d\mathbf{r} \int d\mathbf{r}' \delta(\mathbf{r} - \mathbf{r}') \frac{1}{2} \nabla_{\mathbf{r}}^2 \gamma_1(\mathbf{r}; \mathbf{r}').$$

11.6 Equation (11.76) provides the definition of $\gamma_2(\mathbf{r}; \mathbf{r}')$, which is related to a density operator for an electron defined in the single electron position space. Find out an exact form of such a density operator, which is normalized and defined in the basis of $|\mathbf{r}; 1\rangle$, the position state of an electron 1.

11.7 Equation (11.75) provides the definition of $\gamma_2(\mathbf{r}, \mathbf{r}'; \mathbf{r}'', \mathbf{r}''')$, which is related to a density operator for two electrons defined in the two electron position space. Find out an exact form of such a density operator, which is normalized and defined in the basis of $|\mathbf{r}; 1\rangle \otimes |\mathbf{r}'; 2\rangle$, the position state of two electrons 1 and 2.

11.8 Find out expressions for the single and two electron densities for the case of N_e electron state represented by the Slater determinant, Eq. (11.4).

Chapter 12
Special Topics



No problem is too small or too trivial if we can really do something about it.

– Richard P. Feynman

Abstract This chapter introduces three special topics as follows: (i) path integral representation of quantum dynamics and equilibrium properties; (ii) open system quantum dynamics and quantum master equation approaches; (iii) Green's function approach. These topics have played important roles in theoretical and computational investigation of quantum processes in complex environments. Some of the core concepts and relations will be derived and explained.

Three special topics being introduced in this chapter serve as important theoretical tools for investigating quantum processes in complex environments and for manipulating quantum effects beyond simple measurement processes. Each of these topics has a long history of its own and has been developed for decades. Thus, even a reasonable overview of these topics requires substantial effort that goes beyond the scope of this book. Rather, a few key concepts, identities, and relations that can help readers gain better understanding and develop reasonable perspective of these topics will be presented. Due to informative nature and incompleteness of presentations here, no summary or problems are provided in this chapter.

12.1 Path Integral Representation

Both the time evolution operator of a quantum system and the density operator of a canonical ensemble can in general be expressed in forms of path integrals [16, 17, 56, 57]. This is because the latter can be obtained from the former by using $t = -i\beta\hbar$. Although development of a path integral expression is possible with respect to any complete basis [17, 57], the most well-known and powerful basis is

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that of position states. Thus, we will consider here only conventional path integrals in position basis.

12.1.1 Real Time Propagator

Take for example the time evolution operator for a time independent Hamiltonian, given by Eq. (2.47), in one dimension. For the corresponding time evolution operator $\hat{U}_H(t)$ defined by Eq. (2.82), let us introduce the following real time propagator between x_i and x_f:

$$P(x_f, t; x_i, 0) \equiv \langle x_f|\hat{U}_H(t)|x_i\rangle = \langle x_f|e^{-it\hat{H}/\hbar}|x_i\rangle. \tag{12.1}$$

The time evolution operator shown above can be expressed as a product of N_p propagators for smaller time steps. Thus,

$$e^{-it\hat{H}/\hbar} = e^{-i\delta t\hat{H}/\hbar}\cdots e^{-i\delta t\hat{H}/\hbar}, \tag{12.2}$$

where $\delta t = t/N_p$. Inserting the identity resolution in position space, Eq. (2.25), $N_p - 1$ times in between each time evolution operator for δt, we can express Eq. (12.1) as

$$P(x_f, t; x_i, 0) = \int dx_1 \cdots \int dx_{N_p-1} \prod_{k=1}^{N_p} P(x_k, t_k; x_{k-1}, t_{k-1}), \tag{12.3}$$

where $x_{N_p} = x_f$, $x_0 = x_i$, and $t_k = t\delta t$ for $k = 0, \cdots, N_p$.

For small enough δt, one can make the following Trotter factorization [58] approximation for each time evolution operator for δt.

$$e^{-i\delta t\hat{H}/\hbar} = e^{-i\delta t\hat{V}/(2\hbar)}e^{-i\delta t\hat{T}/\hbar}e^{-i\delta t\hat{V}/(2\hbar)} + O(\delta t^3), \tag{12.4}$$

where $O(\delta t^3)$ implies that the error for the above Trotter factorization is of order δt^3. Within this approximation, the corresponding propagator can be calculated employing the identity resolution in the momentum space, Eq. (2.34), as follows:

$$P(x_k, t_k; x_{k_1}, t_{k-1}) \approx \int_{-\infty}^{\infty} dp\ \langle x_k|e^{-i\delta t\hat{V}/(2\hbar)}|p\rangle\langle p|e^{-i\delta t\hat{T}/\hbar}e^{-i\delta t\hat{V}/(2\hbar)}|x_{k-1}\rangle$$

$$= e^{-i\delta t(V(x_k)+V(x_{k-1}))/(2\hbar)} \int_{-\infty}^{\infty} dp\ \langle x_k|p\rangle e^{-i\delta t p^2/(2m\hbar)}\langle p|x_{k-1}\rangle$$

$$= e^{-i\delta t(V(x_k)+V(x_{k-1}))/(2\hbar)} \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dp\ e^{-i\delta t p^2/(2m\hbar)+i(x_k-x_{k-1})p/\hbar}. \tag{12.5}$$

In the last equality of the above expression, Eq. (2.36) and its complex conjugate have been used.

Note that the integration over momentum in the above expression can be done by completing the square in the exponent and conducting Gaussian integration as follows:

$$\begin{aligned}
&\int_{-\infty}^{\infty} dp\; e^{-i\delta t p^2/(2m\hbar)+i(x_k-x_{k-1})p/\hbar} \\
&= e^{im(x_k-x_{k-1})^2/(2\hbar\delta t)} \int_{-\infty}^{\infty} dp\; e^{-i\delta t/(2m\hbar)(p-m(x_k-x_{k-1})/\delta t)^2} \\
&= \sqrt{\frac{2\pi m\hbar}{i\delta t}} e^{im(x_k-x_{k-1})^2/(2\hbar\delta t)}.
\end{aligned} \tag{12.6}$$

Employing the above identity in Eq. (12.5), we obtain

$$P(x_k, t_k; x_{k_1}, t_{k-1}) = \sqrt{\frac{m}{2i\pi\hbar\delta t}} e^{im(x_k-x_{k-1})^2/(2\hbar\delta t)-i\delta t(V(x_k)+V(x_{k-1}))/(2\hbar)} + O(\delta t^3). \tag{12.7}$$

As is clear from the second term, the error involved in using the first term in the above expression is of order $\delta t^3 = (t/N_P)^3$. When this expression is used in Eq. (12.3), this error is added N_p times and the net error of the resulting expression is of order t^3/N_P^2. Thus, Eq. (12.3) can be expressed as

$$P(x_f, t; x_i, 0) = \left(\frac{mN_p}{2i\pi\hbar t}\right)^{\frac{N_p}{2}} \int dx_1 \cdots \int dx_{N_P-1}\; e^{i\mathcal{A}_{N_p}(\mathbf{x}_{N_p})/\hbar} + O\left(\frac{t^3}{N_p^2}\right), \tag{12.8}$$

where $\mathbf{x}_{N_p} \equiv (x_0, x_1, x_2, \cdots, x_{N_p})$, the vector of discrete position trajectories from $x_0 = x_i$ at $t = 0$ to $x_{N_P} = x_f$ at t, and $\mathcal{A}_{N_p}(\mathbf{x}_{N_p})$ is a function of this vector defined as

$$\begin{aligned}
\mathcal{A}_{N_p}(\mathbf{x}_{N_p}) &\equiv \sum_{k=1}^{N_p} \left\{ \frac{m(x_k - x_{k-1})^2}{2\delta t} - \frac{V(x_k) + V(x_{k-1})}{2}\delta t \right\} \\
&= \delta t \left[\sum_{k=1}^{N_p} \left\{ \frac{m}{2}\left(\frac{x_k - x_{k-1}}{\delta t}\right)^2 - V(x_k) \right\} - \frac{V(x_0) + V(x_{N_p})}{2} \right].
\end{aligned} \tag{12.9}$$

Let us now consider the limit of $N_P \to \infty$, for which $\mathbf{x}_{N_p}$ becomes a continuous trajectory of time $x(t)$ and Eq. (12.9) becomes the following functional of the trajectory known as action functional:

$$\lim_{N_P \to \infty} \mathcal{A}_{N_p}(\mathbf{x}_{N_p}) = \mathcal{A}[x(\cdot); t] \equiv \int_0^t d\tau \left\{ \frac{m}{2} \left(\frac{dx(\tau)}{d\tau} \right)^2 - V(x(\tau)) \right\}. \tag{12.10}$$

In the above expression, $x(\cdot)$ represents a given function $x(\tau)$ as a whole defined for the entire domain of time, τ. The dot $\cdot$ is used as an argument here to distinguish it from a particular value of the function at a certain time t.

Let us also define the following path integral as the limit of the multidimensional integration in Eq. (12.8) as follows:

$$\lim_{N_P \to \infty} \left(\frac{mN_p}{2i\pi\hbar t} \right)^{\frac{N_P}{2}} \int dx_1 \cdots \int dx_{N_P-1} (\cdots) = \int_{x(0)=x_i}^{x(t)=x_f} \mathcal{D}x(\cdot)(\cdots), \tag{12.11}$$

where dots within parentheses imply any functional that is well defined and remains integrable as the discrete trajectory becomes continuous. Whether this limit of path integration is well defined is a nontrivial mathematical issue and also has practical significance. For example, for a free particle or a particle subject to a potential bounded from below, it is generally accepted that the path integral is well-defined as the limit of the multidimensional integration. However, for singular potentials such as Coulomb potential, it is not the case and more careful definition of the measure of integration[1] becomes necessary [17].

Since t^3/N_P^2 becomes zero in the limit of $N_P \to \infty$ for any finite value of t, the error term in Eq. (12.8) becomes zero in that limit. Thus, we obtain the following path integral expression for the propagator:

$$P(x_f, t; x_i, 0) = \int_{x(0)=x_i}^{x(t)=x_f} \mathcal{D}x(\cdot) e^{i\mathcal{A}[x(\cdot);t]/\hbar}. \tag{12.12}$$

Noting the definition of the propagator, Eq. (12.1), the above expression can now be used to obtain the following expression for the real time propagator:

$$\hat{U}_H(t) = \int dx_f \int dx_i \left(\int_{x(0)=x_i}^{x(t)=x_f} \mathcal{D}x(\cdot) e^{i\mathcal{A}[x(\cdot);t]/\hbar} \right) |x_f\rangle\langle x_i|. \tag{12.13}$$

[1] Even for integration of functions, this is an important issue because there are kinds of singular functions for which conventional Riemann measure integration fails but more elaborate Lebesgue measure produces convergent result.

Employing the above expression and its Hermitian conjugate in Eq. (10.45), the time dependent density operator can now be expressed as

$$\hat{\rho}(t) = \int dx_f \int dx_i \int dx'_f \int dx'_i \; |x_f\rangle\langle x_i|\hat{\rho}|x'_i\rangle\langle x'_f| \\ \times \left(\int_{x(0)=x_i}^{x(t)=x_f} \mathcal{D}x(\cdot) \int_{x'(0)=x'_i}^{x'(t)=x'_f} \mathcal{D}x'(\cdot) \; e^{i(\mathcal{A}[x(\cdot);t]-\mathcal{A}[x'(\cdot);t])/\hbar} \right). \tag{12.14}$$

Accordingly, the time dependent average for any operator $\hat{O}$, as defined by Eq. (10.48), with $\hat{\rho}$ replaced by $\hat{\rho}(t)$, can be expressed as

$$\begin{aligned} \langle \hat{O}(t)\rangle &= Tr\left\{\hat{O}\hat{\rho}(t)\right\} \\ &= \int dx \; \langle x|\hat{O}\hat{\rho}(t)|x\rangle \\ &= \int dx_f \int dx_i \int dx'_f \int dx'_i \; \langle x'_f|\hat{O}|x_f\rangle\langle x_i|\hat{\rho}|x'_i\rangle \\ &\quad \times \left(\int_{x(0)=x_i}^{x(t)=x_f} \mathcal{D}x(\cdot) \int_{x'(0)=x'_i}^{x'(t)=x'_f} \mathcal{D}x'(\cdot) \; e^{i(\mathcal{A}[x(\cdot);t]-\mathcal{A}[x'(\cdot);t])/\hbar} \right). \end{aligned} \tag{12.15}$$

In the second equality of the above expression, $\langle x'_f|x\rangle = \delta(x'_f - x)$ has been used.

Extension of expressions derived here to general multidimensional Cartesian coordinates is straightforward [17, 57]. However, for curvilinear coordinates or for cases with cyclic coordinates such as angles, care should be taken for proper definition of path measures [17].

12.1.2 Imaginary Time Propagator

Let us consider the canonical equilibrium density operator, Eq. (10.63), which can also be expressed as

$$\hat{\rho}_\beta = \frac{e^{-i(-i\hbar\beta)\hat{H}/\hbar}}{Tr\left\{e^{-i(-i\hbar\beta)\hat{H}/\hbar}\right\}}. \tag{12.16}$$

Thus, the path integral expression for the canonical equilibrium density operator can be obtained by simply replacing t with $-i\hbar\beta$. Let us introduce an imaginary time t_I such that

$$t = -it_I, \ 0 \le t_I \le \hbar\beta \tag{12.17}$$

Then, the definition of the real time propagator, Eq. (12.1), can be extended to an imaginary time propagator as follows:

$$\langle x_f|e^{-\beta\hat{H}}|x_i\rangle = P(x_f, -i\beta\hbar; x_i, 0) = \langle x_f|e^{-i(-i\beta\hbar)\hat{H}/\hbar}|x_i\rangle. \tag{12.18}$$

Thus, the action given by Eq. (12.9) can be extended to the imaginary time at $t_I = \beta\hbar$, by simply replacing the time integration variable τ with $-i\tau$ and also introducing $x_e(\tau) \equiv x(-i\tau)$, as follows:

$$\begin{aligned}\mathcal{A}[x(\cdot); \beta\hbar] &= -i\int_0^{\beta\hbar} d\tau \left\{\frac{m}{2}\left(\frac{dx_e(\tau)}{-id\tau}\right)^2 - V(x_e(\tau))\right\} \\ &= i\int_0^{\beta\hbar} d\tau \left\{\frac{m}{2}\left(\frac{dx_e(\tau)}{d\tau}\right)^2 + V(x_e(\tau))\right\} \equiv i\mathcal{E}[x_e(\cdot); \beta\hbar],\end{aligned} \tag{12.19}$$

where $\mathcal{E}[x_e(\cdot); \beta\hbar]$ is called Euclidean action and is equal to the average energy along the path time leading to $\beta\hbar$. Note that $x_e(\tau)$ and $x(-i\tau)$ are the same except that the former is viewed as a function of a real valued parameter τ whereas the latter is viewed as that of an imaginary time $-i\tau$. Thus, the imaginary time propagator defined by Eq. (12.18) can be expressed by the following path integral form:

$$\langle x_f|e^{-\beta\hat{H}}|x_i\rangle = \int_{x_e(0)=x_i}^{x_e(\beta\hbar)=x_f} \mathcal{D}x_e(\cdot)\ e^{-\mathcal{E}[x_e(\cdot);\beta\hbar]/\hbar}, \tag{12.20}$$

where the detailed form of the path integral measure can be obtained by using $t = -i\beta\hbar$ in Eq. (12.11) and is given by

$$\int_{x_e(0)=x_i}^{x_e(\beta\hbar)=x_f} \mathcal{D}x_e(\cdot)(\cdots) \equiv \lim_{N_P\to\infty}\left(\frac{mN_p}{2\pi\beta\hbar^2}\right)^{\frac{N_p}{2}} \int dx_1 \cdots \int dx_{N_P-1}(\cdots). \tag{12.21}$$

Equations (12.20) and (12.21) complete the derivation of the path integral representation for the imaginary time propagator. Alternatively, these expressions can be obtained directly by expressing $e^{-\beta\hat{H}}$ as a product of those for higher temperature, $e^{-\epsilon\hat{H}}$, where $\epsilon = \beta/N_P = 1/(k_BTN_P)$. Application of the Trotter factorization for each of $e^{-\epsilon\hat{H}}$ as in Eq. (12.4), conducting Gaussian integration as in Eq. (12.6), but for $\delta t = -i\beta\hbar/N_P$, and sending the limit of $N_P \to \infty$ directly leads to Eqs. (12.20) and (12.21).

Employing Eq. (12.20) for $x_f = x'$ and $x_i = x''$, the unnormalized canonical density operator can be expressed as

$$e^{-\beta\hat{H}} = \int dx' \int dx'' |x'\rangle\langle x''| \left(\int_{x_e(0)=x''}^{x_e(\beta\hbar)=x'} \mathcal{D}x_e(\cdot)\; e^{-\mathcal{E}[x_e(\cdot);\beta\hbar]/\hbar} \right). \tag{12.22}$$

Taking the trace of this, we also obtain the following path integral expression for the partition function:

$$\begin{aligned} Z_\beta = Tr\left\{e^{-\beta\hat{H}}\right\} &= \int dx' \langle x'|e^{-\beta\hat{H}}|x'\rangle \\ &= \int dx' \int_{x(0)=x'}^{x(t)=x'} \mathcal{D}x_e(\cdot)\; e^{-\mathcal{E}[x_e(\cdot);\beta\hbar]/\hbar} \\ &\equiv \oint \mathcal{D}x(\cdot)\; e^{-\mathcal{E}[x_e(\cdot);\beta\hbar]/\hbar}, \end{aligned} \tag{12.23}$$

where the path integration in the last line represents sum over all the cyclic paths that end at the same position as the starting point. Combining Eqs. (12.22) and (12.23), we thus obtain the following path integral expression for the canonical equilibrium density operator:

$$\hat{\rho}_\beta = \frac{e^{-\beta\hat{H}}}{Z_\beta} = \frac{\int dx' \int dx'' |x'\rangle\langle x''| \left(\int_{x_e(0)=x''}^{x_e(\beta\hbar)=x'} \mathcal{D}x_e(\cdot)\; e^{-\mathcal{E}[x_e(\cdot);\beta\hbar]/\hbar} \right)}{\oint \mathcal{D}x(\cdot)\; e^{-\mathcal{E}[x_e(\cdot);\beta\hbar]/\hbar}}. \tag{12.24}$$

Therefore, the average of any operator over the canonical ensemble can be expressed as

$$Tr\left\{\hat{O}\hat{\rho}_\beta\right\} = \frac{\int dx' \int dx'' \langle x''|\hat{O}|x'\rangle \left(\int_{x_e(0)=x''}^{x_e(\beta\hbar)=x'} \mathcal{D}x_e(\cdot)\; e^{-\mathcal{E}[x_e(\cdot);\beta\hbar]/\hbar} \right)}{\oint \mathcal{D}x(\cdot)\; e^{-\mathcal{E}[x_e(\cdot);\beta\hbar]/\hbar}}. \tag{12.25}$$

Extension of the expressions derived above to the case of multidimensional Cartesian coordinate system is straightforward [17, 57]. As is the case with the time evolution operator, mathematical difficulty arises in identifying correct path measure for curvilinear or cyclic coordinates [17].

12.2 Quantum Master Equation for Open System Quantum Dynamics

Consider a quantum system interacting with its environment. Assume that we are interested only in the net effects of the environment on the system and are not concerned about details of the environment. For these cases, it may be possible

to develop ways to consider a reduced quantum dynamics for the system only while only accounting for the net effects of the environment on the system. To what extent is this approach feasible? How can one identify the whole environment and its interaction with the system of interest? These are some of difficult and fundamental questions that still remain active issues of research in open system quantum dynamics. However, in this section, we will bypass asking such questions and simply assume that it is possible to identify the environment, which will be called bath, and its interaction with the system of interest.

To be more specific, let us assume that it is possible to identify a well-defined system Hamiltonian $\hat{H}_s$, a bath Hamiltonian $\hat{H}_b$, and a system-bath interaction Hamiltonian $\hat{H}_{sb}$, which are all defined in the direct product space of the system and the bath and can be added together to define a total Hamiltonian as follows:

$$\hat{H} = \hat{H}_s + \hat{H}_{sb} + \hat{H}_b = \hat{H}_0 + \hat{H}_1, \tag{12.26}$$

where, in the second equality, we have also introduced the zeroth order reference Hamiltonian, $\hat{H}_0$, and the first order term $\hat{H}_1$ that is assumed to be small[2] compared to $\hat{H}_0$. Definitions of these can vary depending on the nature of the problem. If $\hat{H}_{sb}$ is small, defining $\hat{H}_0 = \hat{H}_s + \hat{H}_b$ and $\hat{H}_1 = \hat{H}_{sb}$ is a natural choice. However, an alternative choice is possible if $\hat{H}_{sb}$ is not small enough.

Given that the system and bath as a whole is completely isolated from the rest of the universe, the time evolution of the total density operator representing the sum of system and bath at time t is determined according to the following quantum Liouville equation:

$$\begin{aligned}\frac{d}{dt}\hat{\rho}(t) &= -i\mathcal{L}\hat{\rho}(t) \\ &= -i\left(\mathcal{L}_s + \mathcal{L}_{sb} + \mathcal{L}_b\right)\hat{\rho}(t) \\ &= -i\left(\mathcal{L}_0 + \mathcal{L}_1\right)\hat{\rho}(t).\end{aligned} \tag{12.27}$$

In the above expression, $\mathcal{L}(\cdots) = [\hat{H}, (\cdots)]/\hbar$ and $\mathcal{L}_\alpha(\cdots) = [\hat{H}_\alpha, (\cdots)]/\hbar$, for each of $\alpha = s, sb, b$, and 0, respectively.

There are two major approaches to reduce the dynamics of the total density operator represented by Eq. (12.27) into that involving only the system degree of freedom. One is to use the path integral influence functional approach, which accounts for the net effect of the bath on the system dynamics in the path integral representation of the density operator. This is a powerful approach that has widely been used in the condensed matter physics and remains a promising approach for simulating molecular systems, but is not described here. Readers can refer to an excellent monograph [59] and a review paper [60] on this approach. The other

[2] The meaning of "small" here is the extension of the concept used in the perturbation theory in that the effects of $\hat{H}_1$ on the eigenstates of $\hat{H}_0$ are small.

approach is to use a quantum master equation (QME) [37, 61–64], which has longer history and has been well-established as one of the most general approaches for investigating open system quantum dynamics.

One of the most systematic approaches to derive QMEs is to employ a projection super-operator in the interaction picture with respect to the zeroth order Hamiltonian. For this, let us first introduce the density operator in the interaction picture with respect to $\hat{H}_0$ as follows:

$$\hat{\rho}_I(t) = e^{i\hat{H}_0 t/\hbar}\hat{\rho}(t)e^{-i\hat{H}_0 t/\hbar}. \tag{12.28}$$

The dynamics of this is governed by the following interaction picture quantum Liouville equation:

$$\begin{aligned}\frac{d}{dt}\hat{\rho}_I(t) &= i\mathcal{L}_0\hat{\rho}_I(t) - e^{i\hat{H}_0 t/\hbar}\left(i\mathcal{L}_0 + i\mathcal{L}_1\right)\hat{\rho}(t)e^{-i\hat{H}_0 t/\hbar} \\ &= -e^{i\hat{H}_0 t/\hbar} i\mathcal{L}_1\hat{\rho}(t)e^{-i\hat{H}_0 t/\hbar} \\ &= -\frac{i}{\hbar}[\hat{H}_{1,I}(t), \rho_I(t)] \equiv -i\mathcal{L}_{1,I}(t)\hat{\rho}_I(t),\end{aligned} \tag{12.29}$$

where $\hat{H}_{1,I}(t) = e^{i\hat{H}_0 t/\hbar}\hat{H}_1 e^{-i\hat{H}_0 t/\hbar}$.

12.2.1 Projection Operator Formalism and Exact Time Evolution Equations for a Projected Density Operator

If only a partial information on the density operator is needed, a projection super-operator $\mathcal{P}$, which is assumed to be time independent, can be introduced such that $\mathcal{P}\hat{\rho}_I(t)$ contains all such information. The complement of the projection super-operator is denoted as $\mathcal{Q} = 1 - \mathcal{P}$. So, let us call $\mathcal{P}\hat{\rho}_I(t)$ the projected part of the density operator and $\mathcal{Q}\hat{\rho}_I(t)$ the unprojected part of the density operator. First, we will show that a general exact time evolution equation involving only the projected part of the density operator can be derived without detailed specification of the form of the projection super-operator. In deriving this, it is convenient to assume that the following identity holds:

$$\mathcal{P}\mathcal{L}_{1,I}(t)\mathcal{P} = 0. \tag{12.30}$$

It is important to note that the above condition is not so restrictive and can always be satisfied by an appropriate definition of $\hat{H}_1$. As will be clear, this identity helps to simplify final expression for the formal solution and its perturbative approximations.

Applying $\mathcal{P}$ on the left-hand side of Eq. (12.29), inserting the identity $\mathcal{P}+\mathcal{Q}=\hat{1}$ between $\mathcal{L}_{1,I}(t)$ and $\hat{\rho}_I(t)$, and employing the identity of Eq. (12.30), we obtain

$$\frac{d}{dt}\mathcal{P}\hat{\rho}_I(t) = -i\mathcal{P}\mathcal{L}_{1,I}(t)\mathcal{Q}\hat{\rho}_I(t). \tag{12.31}$$

Similarly, applying $\mathcal{Q}$ on the left-hand side of Eq. (12.29) and inserting the identity of $\mathcal{P}+\mathcal{Q}=\hat{1}$, we also obtain

$$\frac{d}{dt}\mathcal{Q}\hat{\rho}_I(t) = -i\mathcal{Q}\mathcal{L}_{1,I}(t)\mathcal{Q}\hat{\rho}_I(t) - i\mathcal{Q}\mathcal{L}_{1,I}(t)\mathcal{P}\hat{\rho}_I(t). \tag{12.32}$$

A formal solution of the above equation can be found easily. For this, it is convenient to introduce time ordered exponential super-operators as described below.

Time Ordered Exponential Super-Operators

Given a certain time dependent super-operator $\mathcal{M}(t)$ such as interaction picture Liouville or projected/unprojected interaction picture Liouville super-operator and for $t \geq 0$, a positively time ordered exponential super-operator is defined as

$$\begin{aligned} e_{(+)}^{-i\int_0^t d\tau \mathcal{M}(\tau)} \equiv\ & 1 - i\int_0^t d\tau\ \mathcal{M}(\tau) \\ & +(-i)^2\int_0^t d\tau \int_0^\tau d\tau' \mathcal{M}(\tau)\mathcal{M}(\tau') \\ & +\cdots \\ & +(-i)^n \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \cdots \int_0^{\tau_{n-1}} d\tau_n \mathcal{M}(\tau_1)\cdots\mathcal{M}(\tau_n) \\ & +\cdots, \end{aligned} \tag{12.33}$$

which satisfies the following time evolution equation:

$$\frac{d}{dt}e_{(+)}^{-i\int_0^t d\tau \mathcal{M}(\tau)} = -i\mathcal{M}(t)e_{(+)}^{-i\int_0^t d\tau \mathcal{M}(\tau)}. \tag{12.34}$$

On the other hand, a negatively time ordered exponential super-operator is defined as

$$\begin{aligned} e_{(-)}^{i\int_0^t d\tau \mathcal{M}(\tau)} \equiv\ & 1 + i\int_0^t d\tau \mathcal{M}(\tau) \\ & +i^2\int_0^t d\tau \int_0^\tau d\tau' \mathcal{M}(\tau')\mathcal{M}(\tau) \end{aligned}$$

(continued)

$$+\cdots$$
$$+i^n \int_0^t d\tau_1 \cdots \int_0^{\tau_1} d\tau_2 \cdots \int_0^{\tau_{n-1}} d\tau_n \mathcal{M}(\tau_n) \cdots \mathcal{M}(\tau_1)$$
$$+\cdots, \tag{12.35}$$

which satisfies the following time evolution equation:

$$\frac{d}{dt} e_{(-)}^{i\int_0^t d\tau \mathcal{M}(\tau)} = i e_{(-)}^{i\int_0^t d\tau \mathcal{M}(\tau)} \mathcal{M}(t). \tag{12.36}$$

The two time ordered exponential super-operators defined above form an inverse relationship as follows:

$$e_{(+)}^{-i\int_0^t d\tau \mathcal{M}(\tau)} e_{(-)}^{i\int_0^t d\tau \mathcal{M}(\tau)} = e_{(-)}^{i\int_0^t d\tau \mathcal{M}(\tau)} e_{(+)}^{-i\int_0^t d\tau \mathcal{M}(\tau)} = \hat{1}. \tag{12.37}$$

Moving the first term on the righthand side of Eq. (12.32) to the lefthand side, and applying $e_{(-)}^{i\int_0^t d\tau \mathcal{Q}\mathcal{L}_{1,I}(\tau)}$, which is defined by Eq. (12.35) for $\mathcal{M}(t) = \mathcal{Q}\mathcal{L}_{1,I}(t)$ on both sides of the equation, we find that

$$\begin{aligned} & e_{(-)}^{i\int_0^t d\tau \mathcal{Q}\mathcal{L}_{1,I}(\tau)} \frac{d}{dt} \mathcal{Q}\hat{\rho}_I(t) + e_{(-)}^{i\int_0^t d\tau \mathcal{Q}\mathcal{L}_{1,I}(\tau)} i\mathcal{Q}\mathcal{L}_{1,I}(t)\mathcal{Q}\hat{\rho}_I(t) \\ & = \frac{d}{dt}\left(e_{(-)}^{i\int_0^t d\tau \mathcal{Q}\mathcal{L}_{1,I}(\tau)} \mathcal{Q}\hat{\rho}_I(t)\right) = -i e_{(-)}^{i\int_0^t d\tau \mathcal{Q}\mathcal{L}_{1,I}(\tau)} \mathcal{Q}\mathcal{L}_{1,I}(t)\mathcal{P}\hat{\rho}_I(t), \end{aligned} \tag{12.38}$$

where the second equality is obtained by using Eq. (12.36) with $\mathcal{M}(t) = \mathcal{Q}\mathcal{L}_{1,I}(t)$. Integrating the above equation over time from 0 to t, we obtain

$$e_{(-)}^{i\int_0^t d\tau \mathcal{Q}\mathcal{L}_{1,I}(\tau)} \hat{\rho}_I(t) - \hat{\rho}_I(0) = -i \int_0^t d\tau e_{(-)}^{i\int_0^\tau d\tau' \mathcal{Q}\mathcal{L}_{1,I}(\tau')} \mathcal{Q}\mathcal{L}_{1,I}(\tau)\mathcal{P}\hat{\rho}_I(\tau). \tag{12.39}$$

Applying $e_{(+)}^{-i\int_0^t d\tau \mathcal{Q}\mathcal{L}_{1,I}(\tau)}$, which is defined by Eq. (12.33) for $\mathcal{M}(t) = \mathcal{Q}\mathcal{L}_{1,I}(t)$, on both sides of the equation, we find that

$$\mathcal{Q}\hat{\rho}_I(t) = -i \int_0^t d\tau\, e_{(+)}^{-i\int_\tau^t d\tau' \mathcal{Q}\mathcal{L}_{1,I}(\tau')} \mathcal{Q}\mathcal{L}_{1,I}(\tau)\mathcal{P}\hat{\rho}_I(\tau) + e_{(+)}^{-i\int_0^t d\tau \mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau)} \mathcal{Q}\hat{\rho}_I(0), \tag{12.40}$$

where the following relationship has been used.

$$e_{(+)}^{-i\int_0^t d\tau \mathcal{Q}\mathcal{L}_{1,I}(\tau)} e_{(-)}^{i\int_0^\tau d\tau' \mathcal{Q}\mathcal{L}_{1,I}(\tau')} = e_{(+)}^{-i\int_\tau^t d\tau \mathcal{Q}\mathcal{L}_{1,I}(\tau)}. \tag{12.41}$$

The validity of Eq. (12.40) as the solution of Eq. (12.32) can also be proven by direct substitution.

Note that Eq. (12.40) expresses $\mathcal{Q}\hat{\rho}_I(t)$ in terms of $\mathcal{P}\hat{\rho}_I(\tau)$ for $0 \le \tau \le t$ and the initial value of the unprojected part of the density operator at $t = 0$. Thus, when this expression is used in Eq. (12.31), we obtain a closed form of differential equation for $\mathcal{P}\hat{\rho}_I(t)$ as summarized below.

Exact Time-Nonlocal Evolution Equation for the Projected Part of the Density Operator

Using Eq. (12.40) in Eq. (12.31), we obtain the following time evolution equation for the projected part of the density operator:

$$\frac{d}{dt}\mathcal{P}\hat{\rho}_I(t) = -\int_0^t d\tau \mathcal{P}\mathcal{L}_{1,I}(t) e_{(+)}^{-i\int_\tau^t d\tau' \mathcal{Q}\mathcal{L}_{1,I}(\tau')} \mathcal{Q}\mathcal{L}_I(\tau)\mathcal{P}\hat{\rho}_I(\tau)$$
$$-i\mathcal{P}\mathcal{L}_{1,I}(t) e_{(+)}^{-i\int_0^t d\tau \mathcal{Q}\mathcal{L}_{1,I}(\tau)} \mathcal{Q}\hat{\rho}(0), \tag{12.42}$$

where the inhomogeneous term (the second term) retains the information on the initial preparation of the system and the bath at $t = 0$. Note that the above expression involves only the positively time ordered exponential super-operator involving $\mathcal{Q}\mathcal{L}_{1,I}(t)$. Thus, as long as this is well defined, the above solution is also well-defined and valid.

The time evolution equation, Eq. (12.42), is non-local in time and shows that even calculating the time derivative of $\mathcal{P}\hat{\rho}_I(t)$ requires full information on its past. This is not unexpected since the effect of the bath on the dynamics of the system builds up over the history of its time evolution. However, it turns out that it is also possible to account for such memory effect employing a fully time local form. This is because the full dynamics for $\hat{\rho}_I(t)$ is unitary and can be reversed backward. That is, one can always find a formally exact solution for Eq. (12.29), which can relate $\hat{\rho}_I(t)$ to $\hat{\rho}_I(\tau)$ for $\tau \le t$ as follows:

$$\hat{\rho}_I(t) = e_{(+)}^{-i\int_\tau^t d\tau' \mathcal{L}_{1,I}(\tau')} \hat{\rho}(\tau). \tag{12.43}$$

Equivalently, one can also find the following relationship:

$$\hat{\rho}_I(\tau) = e_{(-)}^{i\int_\tau^t d\tau' \mathcal{L}_{1,I}(\tau')} \hat{\rho}_I(t). \tag{12.44}$$

Employing the above identity in Eq. (12.40), we find that

$$\mathcal{Q}\hat{\rho}_I(t) = -i\int_0^t d\tau e_{(+)}^{-i\int_\tau^t d\tau' \mathcal{Q}\mathcal{L}_{1,I}(\tau')}\mathcal{Q}\mathcal{L}_{1,I}(\tau)\mathcal{P}e_{(-)}^{i\int_\tau^t d\tau' \mathcal{L}_{1,I}(\tau')}\hat{\rho}_I(t)$$
$$+e_{(+)}^{-i\int_0^t d\tau \mathcal{Q}\mathcal{L}_{1,I}(\tau)}\mathcal{Q}\hat{\rho}(0). \quad (12.45)$$

Inserting $\mathcal{P}+\mathcal{Q}=\hat{1}$ in front of $\hat{\rho}_I(t)$ on the righthand side of the above equation results in two terms. One involves $\mathcal{P}\hat{\rho}_I(t)$ and the other involves $\mathcal{Q}\hat{\rho}_I(t)$. Moving the term involving the latter to the lefthand side of the equation and applying the inverse[3] of the entire operator being applied to $\mathcal{Q}\hat{\rho}_I(t)$ [65], we now obtain the following key relationship:

$$\mathcal{Q}\hat{\rho}_I(t) = (1+i\Gamma_{1,I}(t))^{-1}$$
$$\times\left\{-i\int_0^t d\tau e_{(+)}^{-i\int_\tau^t d\tau' \mathcal{Q}\mathcal{L}_{1,I}(\tau')}\mathcal{Q}\mathcal{L}_{1,I}(\tau)\mathcal{P}e_{(-)}^{i\int_\tau^t d\tau' \mathcal{L}_{1,I}(\tau')}\mathcal{P}\hat{\rho}_I(t)\right.$$
$$\left.+e_{(+)}^{-i\int_0^t d\tau \mathcal{Q}\mathcal{L}_{1,I}(\tau)}\mathcal{Q}\hat{\rho}(0)\right\}, \quad (12.46)$$

where

$$\Gamma_{1,I}(t) = \int_0^t d\tau e_{(+)}^{-i\int_\tau^t d\tau' \mathcal{Q}\mathcal{L}_{1,I}(\tau')}\mathcal{Q}\mathcal{L}_{1,I}(\tau)\mathcal{P}e_{(-)}^{i\int_\tau^t d\tau' \mathcal{L}_{1,I}(\tau')}. \quad (12.47)$$

Equation (12.46) can be combined with Eq. (12.31), to find an exact time-local equation governing the dynamics of $\mathcal{P}\hat{\rho}_I(t)$ as summarized below.

Exact Time-Local Equation for the Projected Part of the Density Operator

Using Eq. (12.46) in Eq. (12.31), we obtain the following time evolution equation for the projected part of the density operator:

$$\frac{d}{dt}\mathcal{P}\hat{\rho}_I(t) = -\mathcal{P}\mathcal{L}_{1,I}(t)(1+i\hat{\Gamma}_{1,I}(t))^{-1}$$
$$\times\int_0^t d\tau e_{(+)}^{-i\int_\tau^t d\tau' \mathcal{Q}\mathcal{L}_{1,I}(\tau')}\mathcal{Q}\mathcal{L}_{1,I}(\tau)\mathcal{P}e_{(-)}^{i\int_\tau^t d\tau' \hat{\mathcal{L}}_{1,I}(\tau')}\mathcal{P}\hat{\rho}_I(t)$$
$$-i\mathcal{P}\mathcal{L}_{1,I}(t)(1+i\Gamma_{1,I}(t))^{-1}e_{(+)}^{-i\int_{t_0}^t d\tau \mathcal{Q}\mathcal{L}_{1,I}(\tau)}\mathcal{Q}\hat{\rho}(0). \quad (12.48)$$

(continued)

[3] It is assumed here that this inverse can always be found.

Note that the righthand side of the above equation involves the information on $\mathcal{P}\hat{\rho}_I(t)$ only at the same time as that for the lefthand side. This is achieved by expressing the information on $\hat{\rho}_I(\tau)$ for $\tau \leq t$ in terms of $\hat{\rho}_I(t)$ by evolving backward in time and then dividing their effects on projected and unprojected parts again. As a result, the final forms of super-operators in the above expression is more complicated than those in Eq. (12.42).

Equations (12.42) and (12.48) are both exact and general for any form of the Liouville and projection super-operators. Alternative methods to derive these equations exist as well. For example, one can employ the generalized cumulant expansion method [66] for the total density operator and then apply chronological time ordering or partial time ordering prescription [67, 68].

12.2.2 Quantum Master Equations for a Reduced System Density Operator

If we are interested in finding out the general information on the system of interest, we need to be able to determine at least the reduced system density operator defined as

$$\hat{\rho}_{s,I}(t) \equiv Tr_b\{\hat{\rho}_I(t)\}. \tag{12.49}$$

For this, we can introduce the following projection super-operator [37, 62–64]:

$$\mathcal{P}(\cdot) \equiv \hat{\rho}_b \otimes Tr_b\left\{(\cdot)\right\} = \hat{\rho}_b Tr_b\left\{(\cdot)\right\}, \tag{12.50}$$

where $\hat{\rho}_b$ is a bath density operator, which is commonly assumed to be an equilibrium density operator, and the second equality is a short notation for the direct product form. In addition, let us define the zeroth order and the first order Hamiltonians as follows:

$$\hat{H}_0 = \hat{H}_s + \hat{H}_b, \tag{12.51}$$

$$\hat{H}_1 = \hat{H}_{sb}. \tag{12.52}$$

Then, the time evolution operator for $\hat{H}_0$ can be expressed as

$$\hat{U}_0(t) = e^{-i\hat{H}_s/\hbar}e^{-i\hat{H}_bt/\hbar}. \tag{12.53}$$

Therefore,

$$\hat{H}_{1,I}(t) = \hat{H}_{sb,I}(t) = e^{i\hat{H}_s t/\hbar} e^{i\hat{H}_b t/\hbar} \hat{H}_{sb} e^{-i\hat{H}_b t/\hbar} e^{-i\hat{H}_s t/\hbar}. \tag{12.54}$$

For the above case, the condition of Eq. (12.30) implies that, for any operator $\hat{O}$ that depends on both system and bath degrees of freedom, the following identity holds.

$$\begin{aligned}
\mathcal{P}\mathcal{L}_{1,I}(t)\mathcal{P}(\hat{O}) &= \frac{1}{\hbar}\hat{\rho}_b Tr_b\left\{\left[\hat{H}_{1,I}(t), \hat{\rho}_b Tr_b\left\{\hat{O}\right\}\right]\right\} \\
&= \frac{1}{\hbar}\hat{\rho}_b\left(Tr_b\left\{\hat{H}_{1,I}(t)\hat{\rho}_b Tr_b\left\{\hat{O}\right\}\right\}\right. \\
&\quad \left. -Tr_b\left\{\hat{\rho}_b Tr_b\left\{\hat{O}\right\}\hat{H}_{1,I}(t)\right\}\right) \\
&= \frac{1}{\hbar}\hat{\rho}_b\left(Tr_b\left\{\hat{H}_{1,I}(t)\hat{\rho}_b\right\} Tr_b\left\{\hat{O}\right\}\right. \\
&\quad \left. -Tr_b\left\{\hat{O}\right\} Tr_b\left\{\hat{\rho}_b\hat{H}_{1,I}(t)\right\}\right) \\
&= \frac{1}{\hbar}\left[\hat{\rho}_b Tr_b\left\{\hat{H}_{1,I}(t)\hat{\rho}_b\right\}, Tr_b\left\{\hat{O}\right\}\right] = 0.
\end{aligned} \tag{12.55}$$

In the second equality of the above equations, the fact that $\hat{\rho}_b$ commutes with $Tr_b\left\{\hat{O}\right\}$, which becomes independent of the bath after trace over the bath has been used. However, note that $Tr_b\left\{\hat{O}\right\}$ and $Tr_b\left\{\hat{H}_{1,I}(t)\hat{\rho}_b\right\}$, which still remain operators in the system space, do not commute in general. Thus, for the identity to hold for any kind of $\hat{O}$, the latter has to become zero as follows:

$$Tr_b\left\{\hat{H}_{1,I}(t)\hat{\rho}_b\right\} = e^{i\hat{H}_s t/\hbar} Tr_b\left\{e^{i\hat{H}_b t/\hbar}\hat{H}_{sb} e^{-i\hat{H}_b t/\hbar}\hat{\rho}_b\right\} e^{-i\hat{H}_s t/\hbar} = 0. \tag{12.56}$$

For $\hat{\rho}_b = e^{-\beta\hat{H}_b}/Tr_b\left\{e^{-\beta\hat{H}_b}\right\}$ or any other form of $\hat{\rho}_b$ that commutes with $\hat{H}_b$, the above condition implies $Tr_b\left\{\hat{H}_{sb}\hat{\rho}_b\right\} = 0$, which means that the average of system-bath interaction over the bath density operator is zero. In case $\hat{H}_{sb}$ does not satisfy this condition, it is always possible to redefine the system Hamiltonian by adding $Tr_b\left\{\hat{H}_{sb}\hat{\rho}_b\right\}$ and then define $\hat{H}_{sb} - Tr_b\left\{\hat{H}_{sb}\hat{\rho}_b\right\}$ as a new system-bath interaction term. Thus, in order to guarantee the condition of Eq. (12.30), here we assume that

$$\left[\hat{H}_b, \hat{\rho}_b\right] = 0, \tag{12.57}$$

$$Tr_b\left\{\hat{H}_{sb}\hat{\rho}_b\right\} = 0. \tag{12.58}$$

12.2.2.1 Formally Exact QMEs

For the present case, the time-nonlocal time evolution equation for the projected part of the density operator, Eq. (12.42), is expressed as

$$\frac{d}{dt}\mathcal{P}\hat{\rho}_I(t) = -\int_0^t d\tau \mathcal{P}\mathcal{L}_{sb,I}(t)\exp_{(+)}\left[-i\int_\tau^t d\tau' \mathcal{Q}\mathcal{L}_{sb,I}(\tau')\right]\mathcal{Q}\mathcal{L}_{sb,I}(\tau)\mathcal{P}\hat{\rho}_I(\tau)$$
$$-i\mathcal{P}\mathcal{L}_{sb,I}(t)\exp_{(+)}\left[-i\int_{t_0}^t d\tau \mathcal{Q}\mathcal{L}_{sb,I}(\tau)\right]\mathcal{Q}\hat{\rho}_I(0), \qquad (12.59)$$

where $\mathcal{L}_{sb,I}(t)(\cdot) \equiv [\hat{H}_{sb,I}(t), (\cdot)]/\hbar$. The above equation can be used to obtain the exact time-nonlocal QME for the reduced system density operator in the interaction picture, as defined by Eq. (12.49).

Exact Time-Nonlocal QME for Reduced System Density Operator

Taking trace of Eq. (12.59) over the bath degrees of freedom, we obtain the following formally exact time-nonlocal QME for reduced system density operator in the interaction picture, $\hat{\rho}_{s,I}(t)$:

$$\frac{d}{dt}\hat{\rho}_{s,I}(t) = -\int_0^t d\tau\, \mathcal{K}_{sb}(t,\tau)\hat{\rho}_{s,I}(\tau) + \mathcal{I}_{c,sb}(t), \qquad (12.60)$$

where

$$\mathcal{K}_{sb}(t,\tau) = Tr_b\left\{\mathcal{L}_{sb,I}(t)e_{(+)}^{-i\int_\tau^t d\tau' \mathcal{Q}\mathcal{L}_{sb,I}(\tau')}\mathcal{Q}\mathcal{L}_{sb,I}(\tau)\hat{\rho}_b\right\}, \qquad (12.61)$$

$$\mathcal{I}_{c,sb}(t) = -iTr_b\left\{\mathcal{L}_{sb,I}(t)e_{(+)}^{-i\int_0^t d\tau \mathcal{Q}\mathcal{L}_{sb,I}(\tau)}\mathcal{Q}\hat{\rho}_I(0)\right\}. \qquad (12.62)$$

In the Schrödinger picture, the corresponding time-nonlocal QME can be obtained by taking derivative of $\hat{\rho}_s(t) = e^{-i\mathcal{L}_s t}\hat{\rho}_{s,I}(t) = e^{-i\hat{H}_s t/\hbar}\hat{\rho}_{s,I}(t)e^{i\hat{H}_s t/\hbar}$ and employing Eq. (12.60). The resulting expression is as follows:

$$\frac{d}{dt}\hat{\rho}_s(t) = -i\mathcal{L}_s\hat{\rho}_s(t) - e^{-i\mathcal{L}_s t}\int_0^t d\tau\, \mathcal{K}_{sb}(t,\tau)\left(e^{i\hat{H}_s\tau/\hbar}\hat{\rho}_s(\tau)e^{-i\hat{H}_s\tau)/\hbar}\right)$$
$$+e^{-i\mathcal{L}_s t}\mathcal{I}_{c,sb}(t). \qquad (12.63)$$

On the other hand, under the same assumptions of Eqs. (12.57) and (12.58), the time-local QME for $\hat{\rho}_{s,I}(t)$, Eq. (12.48), is expressed as

$$
\begin{aligned}
\frac{d}{dt}\mathcal{P}\hat{\rho}_I(t) = &-\mathcal{P}\mathcal{L}_{sb,I}(t)(1+i\Gamma_{sb,I}(t))^{-1} \\
&\times \int_0^t d\tau e_{(+)}^{-i\int_\tau^t d\tau'\mathcal{Q}\mathcal{L}_{sb,I}(\tau')}\mathcal{Q}\mathcal{L}_{sb,I}(\tau)\mathcal{P}e_{(-)}^{i\int_\tau^t d\tau'\mathcal{L}_{sb,I}(\tau')}\mathcal{P}\rho_I(t) \\
&-i\mathcal{P}\mathcal{L}_{sb,I}(t)(1+i\Gamma_{sb,I}(t))^{-1}e_{(+)}^{-i\int_0^t d\tau\mathcal{Q}\hat{\mathcal{L}}_{sb,I}(\tau)}\mathcal{Q}\hat{\rho}(0).
\end{aligned}
\tag{12.64}
$$

where $\Gamma_{sb,I}(t)$ is defined by Eq. (12.47) with $\mathcal{L}_{1,I}(t)$ replaced by $\mathcal{L}_{sb,I}(t)$. The exact time-local QME for $\hat{\rho}_{s,I}(t)$ thus can be obtained easily from the above equation as summarized below.

Exact Time-Local QME for Reduced System Density Operator

Taking trace of Eq. (12.64) over the bath degrees of freedom, we obtain the following exact time-local QME for the reduced system density operator in the interaction picture:

$$
\frac{d}{dt}\hat{\rho}_{s,I}(t) = -\mathcal{R}_{sb}(t)\hat{\rho}_{s,I}(t) + \mathcal{I}_{l,sb}(t), \tag{12.65}
$$

where

$$
\begin{aligned}
\mathcal{R}_{sb}(t) = \int_0^t d\tau Tr_b\Big\{&\mathcal{L}_{sb,I}(t)(1+i\Gamma_{sb,I}(t))^{-1} \\
&\times e_{(+)}^{-i\int_\tau^t d\tau'\mathcal{Q}\mathcal{L}_{sb,I}(\tau')}\mathcal{Q}\mathcal{L}_{sb,I}(\tau)\mathcal{P}e_{(-)}^{i\int_\tau^t d\tau'\mathcal{L}_{sb,I}(\tau')}\hat{\rho}_b\Big\},
\end{aligned}
\tag{12.66}
$$

$$
\mathcal{I}_{l,sb}(t) = -iTr_b\Big\{\mathcal{L}_{sb,I}(t)(1+i\Gamma_{sb,I}(t,t_0))^{-1}e_{(+)}^{-i\int_0^t d\tau\mathcal{Q}\mathcal{L}_{sb,I}(\tau)}\mathcal{Q}\hat{\rho}(0)\Big\}. \tag{12.67}
$$

In the Schrödinger picture, the corresponding time-local QME can be obtained by taking the derivative of $\hat{\rho}_s(t) = e^{-i\mathcal{L}t}\hat{\rho}_{s,I}(t) = e^{-i\hat{H}_s t/\hbar}\hat{\rho}_{s,I}(t)e^{i\hat{H}_s t/\hbar}$ and employing Eq. (12.65). The resulting expression is

$$
\begin{aligned}
\frac{d}{dt}\hat{\rho}_s(t) = &-i\mathcal{L}_s\hat{\rho}_s(t) - e^{-i\mathcal{L}_s t}\mathcal{R}_{sb}(t)\left(e^{i\hat{H}_s t/\hbar}\hat{\rho}_s(t)e^{-i\hat{H}_s t/\hbar}\right) \\
&+e^{-i\mathcal{L}_s t}\mathcal{I}_{l,sb}(t).
\end{aligned}
\tag{12.68}
$$

12.2.2.2 Second Order QMEs

The kernel in time-nonlocal QME, the relaxation super-operator in time-local QME, and the inhomogeneous terms in both equations can be expanded in terms of $\hat{H}_{sb,I}(t)$. The lowest order approximations with respect to $\hat{H}_{sb,I}(t)$ for both equations in the interaction picture are of second order.

Let us first consider the time-nonlocal QME, Eq. (12.60). Keeping only terms up to the second order of $\mathcal{L}_{sb,I}(t)$ in Eqs. (12.61) and (12.62), and employing the identity of Eq. (12.30), we obtain the following second order approximations for the terms involved in the time-nonlocal QME,

$$\mathcal{K}_{sb}^{(2)}(t,\tau) = Tr_b\left\{\mathcal{L}_{sb,I}(t)\mathcal{L}_{sb,I}(\tau)\hat{\rho}_b\right\}, \tag{12.69}$$

$$\begin{aligned}\mathcal{I}_{c,sb}^{(2)}(t) &= -iTr_b\left\{\hat{\mathcal{L}}_{sb,I}(t)\hat{\rho}_I(0)\right\} \\ &\quad -\int_0^t d\tau Tr_b\left\{\mathcal{L}_{sb,I}(t)\mathcal{L}_{sb,I}(\tau)\mathcal{Q}\hat{\rho}_I(0)\right\}.\end{aligned} \tag{12.70}$$

For the time-local QME, Eq. (12.65), similar 2nd order approximations can be made in Eqs. (12.66) and (12.67) as follows:

$$\mathcal{R}_{sb}^{(2)}(t) = \int_0^t d\tau\ Tr_b\left\{\mathcal{L}_{sb,I}(t)\mathcal{L}_{sb,I}(\tau)\hat{\rho}_b\right\} = \int_0^t d\tau\ \mathcal{K}_{sb}^{(2)}(t,\tau), \tag{12.71}$$

$$\begin{aligned}\mathcal{I}_{l,sb}^{(2)}(t) &= -iTr_b\left\{\mathcal{L}_{sb,I}(t)(1-i\Gamma_{sb,I}^{(1)}(t))\mathcal{Q}\hat{\rho}_I(0)\right\} \\ &\quad -\int_0^t d\tau Tr_b\left\{\mathcal{L}_{sb,I}(t)\mathcal{Q}\mathcal{L}_{sb,I}(\tau)\mathcal{Q}\hat{\rho}_I(0)\right\}.\end{aligned} \tag{12.72}$$

In the above expression, $\Gamma_{sb,I}^{(1)}(t) = \int_{t_0}^t d\tau \mathcal{Q}\mathcal{L}_{sb,I}(\tau)\mathcal{P}$. Clearly, $\Gamma_{sb,I}^{(1)}(t)\mathcal{Q}\hat{\rho}_I(0) = 0$ because $\mathcal{P}\mathcal{Q} = 0$. Therefore,

$$\begin{aligned}\mathcal{I}_{l,sb}^{(2)}(t) &= -iTr_b\left\{\hat{\mathcal{L}}_{sb,I}(t)\hat{\rho}_I(0)\right\} - \int_{t_0}^t d\tau Tr_b\left\{\mathcal{L}_{sb,I}(t)\mathcal{L}_{sb,I}(\tau)\mathcal{Q}\hat{\rho}_I(t_0)\right\} \\ &= \mathcal{I}_{c,sb}^{(2)}(t).\end{aligned} \tag{12.73}$$

Thus, the relaxation super-operator for the 2nd order time-local QME is equal to the integration of the kernel of the 2nd order time-nonlocal QME, while the inhomogeneous terms for both equations are the same.

In the Schrödinger picture, the corresponding second order equations can be obtained by using the above second order approximations in Eqs. (12.63)

and (12.68). Before presenting these equations, it is instructive to consider a generic form of the system-bath interaction Hamiltonian given by

$$\hat{H}_{sb} = \sum_n \hat{S}_n \hat{B}_n, \tag{12.74}$$

where $\hat{S}_n$ and $\hat{B}_n$ are not necessarily Hermitian. Since $\hat{H}_{sb}$ is Hermitian, this means that the sum should also includes those for Hermitian conjugates of $\hat{S}_n$ and $\hat{B}_n$ in such cases. With this convention, $\hat{H}_{sb}$ given by Eq. (12.74) can now represent a wide range of system-bath interactions.

In the interaction picture,

$$\hat{H}_{sb,I}(t) = \sum_n \hat{S}_{n,I}(t)\hat{B}_{n,I}(t). \tag{12.75}$$

where

$$\hat{S}_{n,I}(t) = e^{i\hat{H}_s t/\hbar}\hat{S}_n e^{-i\hat{H}_s t/\hbar}, \tag{12.76}$$

$$\hat{B}_{n,I}(t) = e^{i\hat{H}_b t/\hbar}\hat{B}_n e^{-i\hat{H}_b t/\hbar}. \tag{12.77}$$

Inserting Eq. (12.75) into Eq. (12.69), we find that

$$\begin{aligned}\mathcal{K}_{sb}^{(2)}(t,\tau)\hat{\rho}_{s,I}(\tau) &= \sum_n\sum_{n'} Tr_b\left\{[\hat{S}_{n,I}(t)\hat{B}_{n,I}(t), [\hat{S}_{n',I}(\tau)\hat{B}_{n',I}(\tau), \hat{\rho}_b\hat{\rho}_{s,I}(\tau)]]\right\}\\ &= \sum_n\sum_{n'}\left\{C_{nn'}^{(2)}(t,\tau)[\hat{S}_{n,I}(t), \hat{S}_{n',I}(\tau)\hat{\rho}_{s,I}(\tau)]\right.\\ &\qquad \left. + C_{n'n}^{(2)}(\tau,t)[\hat{\rho}_{s,I}(\tau)\hat{S}_{n',I}(\tau), \hat{S}_{n,I}(t)]\right\},\end{aligned} \tag{12.78}$$

with

$$C_{nn'}^{(2)}(t,\tau) = \frac{1}{\hbar^2} Tr_b\{\hat{B}_{n,I}(t)\hat{B}_{n',I}(\tau)\hat{\rho}_b\}. \tag{12.79}$$

In the second equality of Eq. (12.78), the fact that $\hat{S}_{n,I}(t)$, $\hat{S}_{n',I}(\tau)$, and $\hat{\rho}_{s,I}(\tau)$ all commute with $\hat{B}_{n,I}(t)$, $\hat{B}_{n',I}(\tau)$, and $\hat{\rho}_b$ and the cyclic invariance in the trace of bath operators have been used. Also, note that the first and second sums in the second equality of Eq. (12.78) are Hermitian conjugates of each other since $C_{nn'}^{(2)}(t,\tau)$ and $C_{n'n}^{(2)}(\tau,t)$ are complex conjugates of each other. Combining Eq. (12.78) with the integrand in the second term on the righthand side of Eq. (12.63), we find that

$$
\begin{aligned}
&e^{-i\mathcal{L}_s t}\mathcal{K}_{sb}^{(2)}(t,\tau)\left(e^{i\hat{H}_s\tau/\hbar}\hat{\rho}_s(\tau)e^{-i\hat{H}_s\tau/\hbar}\right)\\
&=\sum_n\sum_{n'}\Big\{C_{nn'}^{(2)}(t,\tau)e^{-i\hat{H}_s t/\hbar}[\hat{S}_{n,I}(t),\hat{S}_{n',I}(\tau)e^{i\hat{H}_s\tau/\hbar}\hat{\rho}_s(\tau)e^{-i\hat{H}_s\tau)/\hbar}]e^{i\hat{H}_s t/\hbar}\\
&\qquad +C_{n'n}^{(2)}(\tau,t)e^{-i\hat{H}_s t/\hbar}[e^{i\hat{H}_s\tau/\hbar}\hat{\rho}_s(\tau)e^{-i\hat{H}_s\tau/\hbar}\hat{S}_{n',I}(\tau),\hat{S}_{n,I}(t)]e^{i\hat{H}_s t/\hbar}\Big\}\\
&=\sum_n\sum_{n'}\Big\{C_{nn'}^{(2)}(t,\tau)[\hat{S}_n,e^{-i\hat{H}_s(t-\tau)/\hbar}\hat{S}_{n'}\hat{\rho}_s(\tau)e^{i\hat{H}_s(t-\tau)/\hbar}]\\
&\qquad +C_{n'n}^{(2)}(\tau,t)[e^{-i\hat{H}_s(t-\tau)/\hbar}\hat{\rho}_s(\tau)\hat{S}_{n'}e^{i\hat{H}_s(t-\tau)/\hbar},\hat{S}_n]\Big\}. \qquad (12.80)
\end{aligned}
$$

Similarly for the second order inhomogeneous term Eq. (12.70), we find that

$$
\begin{aligned}
\mathcal{I}_{c,sb}^{(2)}(t) &= -i\sum_n\left[\hat{S}_{n,I}(t),\hat{\mathcal{F}}_n^{(1)}(t)\right]\\
&\quad -\sum_n\sum_{n'}\int_0^t d\tau\ \left(\left[\hat{S}_{n,I}(t),\hat{S}_{n',I}(\tau)\hat{\mathcal{F}}_{nn'}^{(2)}(t,\tau)\right]\right.\\
&\quad \left.+\left[\hat{\mathcal{F}}_{n'n}^{(2)}(\tau,t)\hat{S}_{n',I}(\tau),\hat{S}_{n,I}(t)\right]\right), \qquad (12.81)
\end{aligned}
$$

where

$$
\hat{\mathcal{F}}_n^{(1)}(t) = \frac{1}{\hbar}Tr_b\{\hat{B}_{n,I}(t)\hat{\rho}_I(0)\}, \qquad (12.82)
$$

$$
\hat{\mathcal{F}}_{nn'}^{(2)}(t,\tau) = \frac{1}{\hbar^2}Tr_b\{\hat{B}_n(t)\hat{B}_{n'}(\tau)\mathcal{Q}\hat{\rho}_I(0)\}. \qquad (12.83)
$$

Note that the above two terms are still operators in the system space. Therefore, the inhomogeneous term in Eq. (12.63) within the second order approximation can be expressed as

$$
\begin{aligned}
e^{-i\mathcal{L}_s t}\mathcal{I}_{c,sb}^{(2)}(t) &= -i\sum_n\left[\hat{S}_n,e^{-i\hat{H}_s t/\hbar}\hat{\mathcal{F}}_n^{(1)}(t)e^{i\hat{H}_s t/\hbar}\right]\\
&\quad -\sum_n\sum_{n'}\int_0^t d\tau\ \left(\left[\hat{S}_n,e^{-i\hat{H}_s(t-\tau)/\hbar}\hat{S}_{n'}\hat{\mathcal{F}}_{nn'}^{(2)}(t,\tau)e^{i\hat{H}_s(t-\tau)/\hbar}\right]\right.\\
&\quad \left.+\left[e^{-i\hat{H}_s(t-\tau)/\hbar}\hat{\mathcal{F}}_{n'n}^{(2)}(\tau,t)\hat{S}_{n'}e^{i\hat{H}_s(t-\tau)/\hbar},\hat{S}_n\right]\right)\\
&\equiv \mathcal{I}^{(2)}(t). \qquad (12.84)
\end{aligned}
$$

Now the general second order time-nonlocal QME for $\hat{H}_{sb}$ given by Eq. (12.74) can be obtained by combining expressions obtained above.

Second Order Time-Nonlocal QME in the Schrödinger Picture

For the type of the system-bath interaction Hamiltonian given by Eq. (12.74), employing Eqs. (12.80) and (12.84) in Eq. (12.63), we obtain the following second order time-nonlocal QME in the Schrödinger picture:

$$\frac{d}{dt}\hat{\rho}_s(t) = -i\mathcal{L}_s\hat{\rho}_s(t) \\ -\sum_n\sum_{n'}\int_0^t d\tau \left\{C^{(2)}_{nn'}(t,\tau)[\hat{S}_n, e^{-i\hat{H}_s(t-\tau)/\hbar}\hat{S}_{n'}\hat{\rho}_s(\tau)e^{i\hat{H}_s(t-\tau)/\hbar}] \right. \\ \left. +C^{(2)}_{n'n}(\tau,t)[e^{-i\hat{H}_s(t-\tau)/\hbar}\hat{\rho}_s(\tau)\hat{S}_{n'}e^{i\hat{H}_s(t-\tau)/\hbar}, \hat{S}_n]\right\} \\ +\mathcal{I}^{(2)}(t). \quad (12.85)$$

For the derivation of the second order time-local equation in the Schrödinger picture, first note that the relaxation super-operator $\mathcal{R}^{(2)}_{sb}(t)$ given by Eq. (12.71) is simply the integration of $\hat{\mathcal{K}}^{(2)}_{sb}(t,\tau)$ over τ. Thus, for $\hat{H}_{sb}$ given by Eq. (12.74), we find that

$$\mathcal{R}^{(2)}_{sb}(t)\hat{\rho}_{s,I}(t) = \sum_n\sum_{n'}\int_0^t d\tau \left\{C^{(2)}_{nn'}(t,\tau)[\hat{S}_{n,I}(t), \hat{S}_{n',I}(\tau)\hat{\rho}_{s,I}(t)] \right. \\ \left. +C^{(2)}_{n'n}(\tau,t)[\hat{\rho}_{s,I}(t)\hat{S}_{n',I}(\tau), \hat{S}_{n,I}(t)]\right\}. \quad (12.86)$$

Therefore, the second term on the righthand side of Eq. (12.68), employing the second order approximation given above, can be expressed as

$$e^{-i\mathcal{L}_st}\mathcal{R}^{(2)}_{sb}(t)\left(e^{i\hat{H}_st/\hbar}\hat{\rho}_s(t)e^{-i\hat{H}_st/\hbar}\right) \\ = \sum_n\sum_{n'}\int_0^t d\tau \left\{C^{(2)}_{nn'}(t,\tau)[\hat{S}_n, e^{-i\hat{H}_s(t-\tau)/\hbar}\hat{S}_{n'}e^{i\hat{H}_s(t-\tau)/\hbar}\hat{\rho}_s(t)] \right. \\ \left. +C^{(2)}_{n'n}(\tau,t)[\hat{\rho}_s(t)e^{-i\hat{H}_s(t-\tau)/\hbar}\hat{S}_{n'}e^{i\hat{H}_s(t-\tau)/\hbar}, \hat{S}_n]\right\}. \quad (12.87)$$

The above expression in combination with the inhomogeneous term leads to a general second order time-local QME as summarized below.

Second Order Time-Local QME in the Schrödinger Picture

For the type of the system-bath interaction Hamiltonian given by Eq. (12.74), employing Eqs. (12.87) and (12.84) in Eq. (12.68), we obtain the following second order time-nonlocal QME in the Schrödinger picture:

$$\begin{aligned}\frac{d}{dt}\hat{\rho}_s(t) &= -i\mathcal{L}_s\hat{\rho}_s(t) \\ &\quad -\sum_n\sum_{n'}\int_0^t d\tau \left\{C^{(2)}_{nn'}(t,\tau)[\hat{S}_n, e^{-i\hat{H}_s(t-\tau)/\hbar}\hat{S}_{n'}e^{i\hat{H}_s(t-\tau)/\hbar}\hat{\rho}_s(t)]\right. \\ &\qquad \left. +C^{(2)}_{n'n}(\tau,t)[\hat{\rho}_s(t)e^{-i\hat{H}_s(t-\tau)/\hbar}\hat{S}_{n'}e^{i\hat{H}_s(t-\tau)/\hbar},\hat{S}_n]\right\} \\ &\quad +\mathcal{I}^{(2)}(t). \end{aligned} \tag{12.88}$$

The approach of deriving second order approximations described above can be extended further to derive higher order perturbative approximations in both time-nonlocal and time-local forms [37, 69, 70]. However, such perturbative expansions result in much more complicated expressions in general while they may not lead to significant improvements. Rather, approaches to account for terms up to the infinite order (in principle) through hierarchy of equations of motion approach [71–74] or an approach to solve unprojected part through numerical solution of integral equation, which is called generalized QME [75, 76], have been more successful. Alternatively, it is possible to account for some higher order terms through unitary transformation that effectively reduces the system-bath interaction, while still using the second order approximation [77, 78].

12.3 Green's Function Approach

Mathematically, Green's function is an inverse of a differential operator and enables finding the solution of an inhomogeneous differential equation employing those for the homogeneous equation [30, 79, 80]. Let us consider the following inhomogeneous differential equation,

$$\hat{L}(\xi)f(\xi) = S(\xi), \tag{12.89}$$

where $\hat{L}(\xi)$ is a differential operator with ξ as a variable and $S(\xi)$ is the source term. Although one dimensional notation is used here, ξ can be multidimensional in general. For example, ξ can represent either the time or spatial coordinates, or both

of them. Green function for the above differential equation is defined as the solution of the following equation with a delta function source term.

$$\hat{L}(\xi)G(\xi, \xi') = \delta(\xi - \xi'). \tag{12.90}$$

Then, the general solution of Eq. (12.89) can be expressed as follows:

$$f(\xi) = f_h(\xi) + \int d\xi' G(\xi, \xi')S(\xi'), \tag{12.91}$$

where $f_h(\xi)$ is the homogeneous solution of the differential equation such that $\hat{L}(\xi) f_h(\xi) = 0$. The fact that $f(\xi)$ given above indeed is a solution of Eq. (12.89) is shown below.

$$\begin{aligned} \hat{L}(\xi)\left(f_h(\xi) + \int ds' G(\xi, \xi')S(\xi')\right) &= \int d\xi' \hat{L}_\xi G(\xi, \xi')S(\xi') \\ &= \int d\xi' \delta(\xi - \xi')S(\xi') = S(\xi). \end{aligned} \tag{12.92}$$

Employing Green's function is convenient because it can incorporate boundary conditions within its form. In addition, solutions involving Green's functions are easier to develop systematic approximations.

Green's function can also be used for obtaining (or approximating) the homogenous solution of a complicated differential operator in terms of those for simpler ones. For example, assume that the differential operator $\hat{L}(\xi)$ can be divided into two terms,

$$\hat{L}(\xi) = \hat{L}_0(\xi) + \hat{L}_1(\xi), \tag{12.93}$$

and that the Green function for $\hat{L}_0(\xi)$, which is denoted as $G_0(\xi, \xi')$, can be obtained easily. Then, the differential equation for the homogeneous solution for $\hat{L}(\xi)$ can be expressed as

$$\hat{L}_0(\xi) f(\xi) = -\hat{L}_1(\xi) f(\xi). \tag{12.94}$$

Treating the righthand side of the above equation as a source term, we can express the solution $f(\xi)$ in term of $G_0(\xi, \xi')$ as

$$f(\xi) = f_0(\xi) - \int ds' G_0(\xi, \xi')\hat{L}_1(\xi') f(\xi'). \tag{12.95}$$

Although the above equation still involves unknown $f(\xi')$ on the righthand side, a formal solution can be obtained by iterating the righthand side as follows:

$$
\begin{aligned}
f(\xi) = f_0(\xi) &- \int d\xi_1 \, G_0(\xi, \xi_1)\hat{L}_1(\xi_1) f_0(\xi_1) \\
&+ \int d\xi_1 \int d\xi_2 \, G_0(\xi, \xi_1)\hat{L}_1(\xi_1) G_0(\xi_1, \xi_2)\hat{L}_1(\xi_2) f_0(\xi_2) \\
&+ \cdots \\
&+ (-1)^n \int d\xi_1 \cdots \int d\xi_n \, G_0(\xi, \xi_1)\hat{L}_1(\xi_1) \cdots G_0(\xi_{n-1}, \xi_n)\hat{L}_1(\xi_n) f_0(\xi_n) \\
&+ \cdots .
\end{aligned}
\tag{12.96}
$$

Given that the above series converge quickly, one can truncate the above expansion at finite order, obtaining a perturbative approximation. More advanced approaches are to employ integral transformation and/or diagrammatic techniques [18] to account for major terms up to an infinite order.

The standard Green's function in quantum mechanics refers to that for the Schrödinger equation and has played an important role in scattering and dynamics problems [3, 17, 81]. In fact, the real and imaginary time propagators defined in the path integral representation can also be viewed as examples of Green's function.

However, more generally, Green's function approach in quantum mechanics often refers to a general class of powerful technique to solve quantum many body problems in combination with quantum field theory [18, 81]. Operational definitions of Green's functions in this approach are correlation functions of field operators, which retain all the major spatiotemporal dynamics of quantum particles in interacting environments and can be used for the calculation of all the relevant physical properties. The remainder of this section will provide a very brief account of this approach, starting from the definition of field operators. For comprehensive accounts of theoretical basis and important technical details of the Green's function approach, readers are strongly recommended to refer to more advanced references [18, 82].

12.3.1 Second Quantization and Field Operators

Let us consider the lowering and raising operators $\hat{b}$ and $\hat{b}^\dagger$ for a harmonic oscillator as defined by Eqs. (3.51) and (3.52) in Chap. 3. The two operators satisfy Eqs. (3.53)–(3.55) and can be used to express the Hamiltonian as Eq. (3.57). For a given eigenstate $|v\rangle$ of the harmonic oscillator, application of $\hat{b}^\dagger$ produces $|v+1\rangle$ according to Eq. (3.67) and application of $\hat{b}$ to $|v\rangle$ produces $|v-1\rangle$ according to Eq. (3.70).

In the second quantization formulation of quantum mechanics, each eigenstate $|v\rangle$ of the harmonic oscillator Hamiltonian can be viewed as a state with v number of phonons. Then, the ground vibrational state $|0\rangle$ can be defined as the "vacuum" state of phonons and $\hat{b}^\dagger$ and $\hat{b}$ now become creation and annihilation operators of phonons. This view of quantum harmonic oscillator is equivalent to the one

described in Chap. 3 and allows expressing all physical observables and states only in terms of products of $\hat{b}$'s and $\hat{b}^\dagger$'s applied to the vacuum state.

The second quantization formulation is particularly useful when there are many (possibly infinite number of) harmonic oscillator normal modes because there is no need to introduce eigenstates with many (possibly infinite number of) indices. Instead, for a system of N_s independent harmonic oscillator normal modes, we can define $\hat{b}_j^\dagger$ and $\hat{b}_j$, with $j = 1, \cdots, N_s$, as the creation and annihilation operators of a phonon for each mode.

Phonons for each mode are identical particles satisfying boson statistics. In fact, the definition of creation and annihilation operators for phonons can be extended to other types of bosons as well. For this, it is first necessary to define the occupation number space of bosons. Let us introduce a state in the occupation number space,

$$|n_1, \cdots, n_k, \cdots, n_{N_s}\rangle : \text{ A quantum state where there are } n_1 \text{ particles in state } 1, \cdots, n_k \text{ particles in state } k, \cdots \text{ and } n_{N_s} \text{ particles in state } N_s \tag{12.97}$$

Then, the creation and annihilation operators for bosons in the kth state, which are in general denoted as $\hat{b}_k^\dagger$ and $\hat{b}_k$, can be defined as described below.

Creation and Annihilation Operators for Bosons

For the state in the occupation number space defined by Eq. (12.97), creation and annihilation operators for bosons in the kth state are defined by

$$\hat{b}_k^\dagger |n_1, \cdots, n_k, \cdots, n_{N_s}\rangle = \sqrt{n_k + 1}|n_1, \cdots, n_k + 1, \cdots, n_{N_s}\rangle, \tag{12.98}$$

$$\hat{b}_k |n_1, \cdots, n_k, \cdots, n_{N_s}\rangle = \sqrt{n_k}|n_1, \cdots, n_k - 1, \cdots, n_{N_s}\rangle, \tag{12.99}$$

and satisfy the following commutator identities:

$$[\hat{b}_j, \hat{b}_k^\dagger] = \delta_{jk}, \tag{12.100}$$

$$[\hat{b}_j^\dagger, \hat{b}_k^\dagger] = [\hat{b}_j, \hat{b}_k] = 0. \tag{12.101}$$

Then, the state in the occupation number space, Eq. (12.97), can be expressed as

$$|n_1, \cdots, n_k, \cdots, n_{N_s}\rangle = \prod_{k=1}^{N_s} \frac{1}{\sqrt{n_k!}} \left(\hat{b}_k^\dagger\right)^{n_k} |vac\rangle, \tag{12.102}$$

where $|vac\rangle$ is the vacuum state without any boson particles occupying the states. Note that the above definition is independent of the order of creation operators for different indices because they commute with each other.

The creation and annihilation operators introduced above define a number operator $\hat{n}_k = \hat{a}_k^\dagger \hat{a}_k$ for bosons in the state k as follows:

$$\hat{b}_k^\dagger \hat{b}_k |n_1, \cdots, n_k, \cdots, n_{N_s}\rangle = n_k |n_1, \cdots, n_k, \cdots, n_{N_s}\rangle, \tag{12.103}$$

which can be shown directly by consecutive applications of Eqs. (12.98) and (12.99).

The creation and annihilation operators defined above can also be used for photons, which are bosons, for each frequency and polarization direction. If photons are confined in a small volume, only certain frequencies satisfying the boundary conditions are allowed. Thus, the states of photons in such case are discrete. However, as the volume becomes infinite, the spectrum of photon frequencies becomes continuous and the corresponding Hamiltonian of light involves integration over the entire frequency range.

For fermions such as electrons, the occupation number state such as Eq. (12.97) can still be used. However, the number of particles in each state can be only either 0 or 1. In addition, exchange of the states of two particles should result in change of the sign of the state. All of these properties can be naturally encoded by defining creation and annihilation operators satisfying different identities as described below.

Creation and Annihilation Operators for Fermions

Creation and annihilation operators for states r and s of fermions, $\hat{a}_r^\dagger$ and $\hat{a}_s$, satisfy the following anti-commutation relationship:

$$\{\hat{a}_r^\dagger, \hat{a}_s\} \equiv \hat{a}_r^\dagger \hat{a}_s + \hat{a}_s \hat{a}_r^\dagger = \delta_{rs}. \tag{12.104}$$

On the other hand, between annihilation or creation operators, the following anti-commutation identities hold.

$$\{\hat{a}_r, \hat{a}_s\} = \{\hat{a}_r^\dagger, \hat{a}_s^\dagger\} = 0. \tag{12.105}$$

Then, the state, Eq. (12.97), can be expressed as

$$|n_1, \cdots, n_r, \cdots, n_{N_s}\rangle = (\hat{a}_1^\dagger)^{n_1} (\hat{a}_2^\dagger)^{n_2} \cdots (\hat{a}_s^\dagger)^{n_s} \cdots (\hat{a}_{N_s}^\dagger)^{n_{N_s}} |vac\rangle, \tag{12.106}$$

where $|vac\rangle$ is the vacuum state without any fermion particles occupying the states and each $n_r = 0$ or 1.

Equation (12.105) for $r = s$ implies that $\hat{a}_s^2 = \hat{a}_s^{\dagger 2} = 0$ for each s. On the other hand, Eq. (12.104) for $r = s$ implies that $\hat{a}_s^\dagger \hat{a}_s = 1 - \hat{a}_s \hat{a}_s^\dagger$. Thus, combining the two cases, we find that

$$(\hat{a}_s^\dagger \hat{a}_s)^2 = \hat{a}_s^\dagger \hat{a}_s - \hat{a}_s^\dagger \hat{a}_s^2 \hat{a}_s^\dagger = \hat{a}_s^\dagger \hat{a}_s. \tag{12.107}$$

The above identity is true only if the eigenvalue of $\hat{a}_s^\dagger \hat{a}_s$ is either 0 or 1. Thus, the number operator for each state s in this case is given by $\hat{n}_s = \hat{a}_s^\dagger \hat{a}_s$ as well. On the other hand, the number operators for different states ($r \neq s$) commute with each other as shown below.

$$\begin{aligned}[\hat{n}_r, \hat{n}_s] &= \hat{a}_r^\dagger \hat{a}_r \hat{a}_s^\dagger \hat{a}_s - \hat{a}_s^\dagger \hat{a}_s \hat{a}_r^\dagger \hat{a}_r = -\hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_r \hat{a}_s - \hat{a}_s^\dagger \hat{a}_s \hat{a}_r^\dagger \hat{a}_r \\ &= \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_s \hat{a}_r - \hat{a}_s^\dagger \hat{a}_s \hat{a}_r^\dagger \hat{a}_r = -\hat{a}_s^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_r - \hat{a}_s^\dagger \hat{a}_s \hat{a}_r^\dagger \hat{a}_r \\ &= \hat{a}_s^\dagger \hat{a}_s \hat{a}_r^\dagger \hat{a}_r - \hat{a}_s^\dagger \hat{a}_s \hat{a}_r^\dagger \hat{a}_r = 0. \end{aligned} \tag{12.108}$$

This means that simultaneous diagonalization of any set of the $\hat{n}_r$ is possible, which validates the occupation number state defined by Eq. (12.106).

In general, creation of a single boson or fermion particle does not have to be limited to a specific state but can be any linear superposition of those for different states. In addition, it is often useful to have a definite spatial information on the created particle because interactions between particles are local in space, in particular, for actual particles such as electrons. For this reason, it is useful to consider a general linear combination of creation or annihilation operators projected onto the position space. These are called field operators and are defined below.

Field Operators

Field operators are linear combinations of creation or annihilation operators defined as

$$\hat{\psi}(\mathbf{r}) = \sum_k \psi_k(\mathbf{r}) \hat{c}_k, \tag{12.109}$$

$$\hat{\psi}^\dagger(\mathbf{r}) = \sum_k \psi_k^\dagger(\mathbf{r}) \hat{c}_k^\dagger, \tag{12.110}$$

where $\hat{c}_k$ and $\hat{c}_k^\dagger$ are annihilation and creation operators for either bosons or fermions, and $\psi_k(\mathbf{r})$ is the wavefunction (or vector of wavefunctions for particles with nonzero spins) for the state k. it is assumed that the summation index k runs over a complete set of single-particle quantum states.

For the case of bosons, the field operators defined above satisfy the following commutator identity:

$$[\hat{\psi}(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')] = \sum_k \sum_{k'} \psi_k(\mathbf{r})\psi^*_{k'}(\mathbf{r}')[\hat{b}_k, \hat{b}^\dagger_{k'}] = \sum_k \psi_k(\mathbf{r})\psi^*_k(\mathbf{r}')$$
$$= \sum_k \langle \mathbf{r}|\psi_k\rangle\langle\psi_k|\mathbf{r}'\rangle = \delta(\mathbf{r} - \mathbf{r}'). \tag{12.111}$$

On the other hand, for fermions with spin half such as electrons, the field operator defined above satisfy the following anti-commutator identity:

$$\left\{\hat{\psi}_\gamma(\mathbf{r}), \hat{\psi}^\dagger_{\gamma'}(\mathbf{r}')\right\} = \sum_k \sum_{k'} \psi_{k,\gamma}(\mathbf{r})\psi^*_{k,\gamma'}(\mathbf{r}') \left\{\hat{a}_k, \hat{a}^\dagger_{k'}\right\} = \sum_k \psi_{k,\gamma}(\mathbf{r})\psi^*_{k,\gamma'}(\mathbf{r}')$$
$$= \delta_{\gamma\gamma'} \sum_k \langle \mathbf{r}|\psi_k\rangle\langle\psi_k|\mathbf{r}'\rangle = \delta_{\gamma\gamma'}\delta(\mathbf{r} - \mathbf{r}'), \tag{12.112}$$

where γ, γ' represent either spin up or down.

The field operators defined above can be used to represent physical observables. For example, the operator for any one-body function given by a sum of all the particles, $A = \sum_j A(\mathbf{r}_j)$, can be expressed as

$$\hat{A} = \int d\mathbf{r}\ \hat{\psi}^\dagger(\mathbf{r})A(\mathbf{r})\hat{\psi}(\mathbf{r}). \tag{12.113}$$

It is also possible to prove that the Hamiltonian operator for identical particles of mass m subject to external potential $v_{ext}(\mathbf{r})$ and with pair-wise interaction potential $V_{int}(\mathbf{r}, \mathbf{r}')$ can be expressed as

$$\hat{H} = \int d\mathbf{r} \int d\mathbf{r}'\ \hat{\psi}^\dagger(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}}\delta(\mathbf{r} - \mathbf{r}')\right) \hat{\psi}(\mathbf{r}') + \int d\mathbf{r}\ \hat{\psi}^\dagger(\mathbf{r})v_{ext}(\mathbf{r})\hat{\psi}(\mathbf{r})$$
$$+\frac{1}{2} \int \int d\mathbf{r} \int d\mathbf{r}'\ \hat{\psi}^\dagger(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r}')V_{int}(\mathbf{r}, \mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r}). \tag{12.114}$$

12.3.2 Ground State (Zero Temperature) Green's Functions

For the total Hamiltonian $\hat{H}$ of an interacting many particle system, let us define time dependent field operators in the Heisenberg picture,

$$\hat{\psi}_{H\gamma}(\mathbf{r}t) = e^{i\hat{H}t/\hbar}\hat{\psi}_\gamma(\mathbf{r})e^{-i\hat{H}t/\hbar}, \tag{12.115}$$

$$\hat{\psi}^\dagger_{H\gamma}(\mathbf{r}t) = e^{i\hat{H}t/\hbar}\hat{\psi}^\dagger_\gamma(\mathbf{r})e^{-i\hat{H}t/\hbar}. \tag{12.116}$$

Then, the single particle Green's function with respect to the normalized ground state $|\Psi_0\rangle$ is defined as

$$G_{\gamma\gamma'}(\mathbf{r}t, \mathbf{r}'t') \equiv -i\langle\Psi_0|\mathcal{T}\left(\hat{\psi}_{H\gamma}(\mathbf{r}, t)\hat{\psi}^{\dagger}_{H\gamma'}(\mathbf{r}', t')\right)|\Psi_0\rangle, \tag{12.117}$$

where $\mathcal{T}$ is the chronological time ordering super-operator. Thus, the above Green's functions can be expressed as

$$G_{\gamma\gamma'}(\mathbf{r}t, \mathbf{r}'t') = \begin{cases} -i\langle\Psi_0|\hat{\psi}_{H\gamma}(\mathbf{r}t)\hat{\psi}^{\dagger}_{H\gamma'}(\mathbf{r}', t')|\Psi_0\rangle \ , t > t' \\ \mp i\langle\Psi_0|\hat{\psi}^{\dagger}_{H\gamma}(\mathbf{r}', t')\hat{\psi}_{H\gamma'}(\mathbf{r}t)|\Psi_0\rangle \ , t' > t \end{cases} \tag{12.118}$$

In the second row on the righthand side of the above equation, the $-$ sign is for bosons and the $+$ sign is for fermions. This sign convention makes the above definition of Green's function consistent with the commutator and anti-commutator identities of bosons and fermions, respectively. Green's functions for two particle field operators can be defined in a similar manner.

The Green's function defined above provides direct information on the excitation properties. For example, in the Fourier transforms of this Green's function with respect to time and position, the location and strength of poles respectively give direct information on excitation energies and strengths. Thus, in combination with powerful diagrammatic techniques [18] and more recently with direct numerical iteration techniques, which allow calculation of Green's functions for interacting many-particle systems from those for simple reference systems, one can calculate the key properties related to ionizations or excitations without going through calculation of many-body wavefunctions.

12.3.3 Nonequilibrium Green's Functions

Nonequilibrium Green's functions serve as important tools for calculating transport properties [83, 84] in open environments including the case where there is particle exchange with reservoir. Within the Keldysh formalism [85], this can be done by defining contour ordered correlation functions of field operators. For this, let us omit writing explicitly the spatial coordinates and denote each operator in terms of time. Let us also drop the subscript H denoting the Heisenberg picture.

For any nonequilibrium process that can be defined to have evolved from an equilibrium grand canonical distribution in the infinite past, one can define the following contour ordered Green's function :

$$G(\tau, \tau') = -i\langle\mathcal{T}_c\left\{\hat{\psi}(\tau)\hat{\psi}^{\dagger}(\tau')\right\}\rangle, \tag{12.119}$$

where $\langle\cdots\rangle$ means trace over the grand canonical density operator at infinite past ($t = -\infty$) and $\mathcal{T}_c$ is the normal time ordering operator along the closed time contour that starts from $-\infty$ to ∞ and then comes back to $-\infty$. In case τ comes later than τ' along the contour, $G(\tau, \tau')$ becomes the following greater Green's function:

$$G^{>}(\tau,\tau') = -i\langle\hat{\psi}(\tau)\hat{\psi}^{\dagger}(\tau')\rangle. \tag{12.120}$$

On the other hand, in case τ' comes later than τ along the contour, $G(\tau,\tau')$ becomes the following lesser Green's function:

$$G^{<}(\tau,\tau') = \mp i\langle\hat{\psi}^{\dagger}(\tau')\hat{\psi}(\tau)\rangle. \tag{12.121}$$

where the $-$ sign is for bosons and $+$ sign is for fermions. Note that these greater and lesser Green's functions are well defined even when the averaging is over the ground state. In fact, the two cases of Eq. (12.118) correspond to these greater and lesser Green's functions.

It is also useful to define retarded and advanced Green's functions as follows:

$$\begin{aligned}G^{r}(\tau,\tau') &= -i\Theta(\tau-\tau')\langle\hat{\psi}(\tau)\hat{\psi}^{\dagger}(\tau')+\hat{\psi}^{\dagger}(\tau')\hat{\psi}(\tau)\rangle \\ &= \Theta(\tau-\tau')\big(G^{>}(\tau,\tau')-G^{<}(\tau,\tau')\big),\end{aligned} \tag{12.122}$$

$$\begin{aligned}G^{a}(\tau,\tau') &= i\Theta(\tau'-\tau)\langle\hat{\psi}(\tau)\hat{\psi}^{\dagger}(\tau')+\hat{\psi}^{\dagger}(\tau')\hat{\psi}(\tau)\rangle \\ &= \Theta(\tau'-\tau)\big(G^{<}(\tau,\tau')-G^{>}(\tau,\tau')\big).\end{aligned} \tag{12.123}$$

Finally, let us also define two regular time ordered Green functions defined along a straight real time line as follows:

$$G^{(+)}(\tau,\tau') = -i\langle\mathcal{T}\Big\{\hat{\psi}(\tau)\hat{\psi}^{\dagger}(\tau')\Big\}\rangle, \tag{12.124}$$

$$G^{(-)}(\tau,\tau') = -i\langle\tilde{\mathcal{T}}\Big\{\hat{\psi}(\tau)\hat{\psi}^{\dagger}(\tau')\Big\}\rangle, \tag{12.125}$$

where $\mathcal{T}$ is the chronological time ordering super-operator and $\tilde{\mathcal{T}}$ is the anti-chronological time ordering super-operator. Then, we can show that

$$G^{(+)}(\tau,\tau') = \Theta(\tau-\tau')G^{>}(\tau,\tau')+\Theta(\tau'-\tau)G^{<}(\tau,\tau'), \tag{12.126}$$

$$G^{(-)}(\tau,\tau') = \Theta(\tau'-\tau)G^{>}(\tau,\tau')+\Theta(\tau-\tau')G^{<}(\tau,\tau'). \tag{12.127}$$

Combining Eqs. (12.122), (12.123), (12.126), and (12.127), we can also establish the following identities:

$$\begin{aligned}G^{<}(\tau,\tau') &= G^{(+)}(\tau,\tau')-G^{r}(\tau,\tau') \\ &= G^{(-)}(\tau,\tau')+G^{a}(\tau,\tau'),\end{aligned} \tag{12.128}$$

$$\begin{aligned}G^{>}(\tau,\tau') &= G^{(+)}(\tau,\tau')-G^{a}(\tau,\tau') \\ &= G^{(-)}(\tau,\tau')+G^{r}(\tau,\tau').\end{aligned} \tag{12.129}$$

A great deal of dynamical properties in nonequilibrium processes can be expressed in terms of the following convolution of contour-order Green's functions:

$$A(\tau, \tau') = \int_c d\tau_1 B(\tau, \tau_1) C(\tau_1, \tau'). \tag{12.130}$$

Langreth [86] showed that the above convolution can be related to those for standard types of Green functions employing a two-looped contour which passes through ∞ twice with t and t' on each loop. Important examples of these are

$$A^<(t, t') = \int_{-\infty}^{\infty} dt_1 \left\{B^r(t, t_1)C^<(t_1, t') + B^<(t, t_1)C^a(t_1, t')\right\}, \tag{12.131}$$

$$A^>(t, t') = \int_{-\infty}^{\infty} dt_1 \left\{B^>(t, t_1)C^a(t_1, t') + B^r(t, t_1)C^>(t_1, t')\right\}, \tag{12.132}$$

$$A^r(t, t') = \int_{-\infty}^{\infty} dt_1 B^r(t, t_1)C^r(t_1, t'), \tag{12.133}$$

$$A^a(t, t') = \int_{-\infty}^{\infty} dt_1 B^a(t, t_1)C^a(t_1, t'). \tag{12.134}$$

Application of the above identities makes it possible to reduce expressions for nonequilibrium transport properties to those involving standard Green's functions that have clear analogues in the equilibrium case and thus can be calculated extending well established techniques for equilibrium Green's functions.

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